

Urea-based moulding compounds for investment casting

By

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ABSTRACT

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Conventional urea-based moulding compounds for investment casting patterns are manufactured using a slow “cooking” process. Nowadays in industrial processes the use of a faster process is highly recommended to increase throughput levels. At the same time, for quality control purposes, the requirements of an investment caster must be met. This study is therefore focused on:

- Finding the appropriate conventional process and conditions to prepare urea-based investment casting moulding compounds.
- Optimising the composition variables to meet the mechanical, thermal, surface, flow and cost properties needed in investment casting.
- Characterising the moulding compounds to meet the requirements of an investment caster by comparing them with an industrial, “cooked” urea-based compound.

Polyvinyl alcohol (PVOH) and ethylene vinyl acetate (EVA) urea-based moulding compounds were prepared using a two-roll mill and a conventional extrusion processes respectively. It was possible to injection mould PVOH urea-based moulding compounds with a urea content of up to 90 wt % which had been compounded using a two-roll mill. Using the conventional extrusion

process, it was also possible to compound and injection mould EVA urea-based moulding compounds containing up to 70 wt % urea.

The effects on composition variables on the properties of the moulding compound were studied and compared to those of the existing “cooked” urea-based moulding compound (Benchmark). The mechanical properties were characterised using the three-point bending test and Charpy impact test. The thermal properties were determined using simultaneous differential thermal analysis and thermogravimetric analysis (SDTA/TGA) and differential scanning calorimeter (DSC). The thermo-mechanical and visco-elastic properties were determined using a dynamic mechanical analyser. A scanning electron microscope was used to study the surface texture of the mouldings.

The EVA urea-based moulding compounds showed two endothermic melting peaks and multiple exothermic crystallisation peaks in the DSC curves. The peak at ca. 55 - 66°C corresponds to the melting of the wax/EVA blend, while the large peak at 130 - 132°C corresponds to the melting of the urea. The DSC heating curve of the PVOH urea-based moulding compounds showed two endothermic peaks. The small peak corresponds to the melting of the wax, while the large peak corresponds to the melting of the urea/PVOH blend.

PVOH urea-based moulding compound had better mechanical properties than the industrial benchmark. The mechanical properties of the EVA urea-based compound were generally lower. The effect of the wax and polymer content on the mechanical properties was as follows:

- Increasing polymer content produced weaker but tougher moulding compounds.
- Increasing wax content improved the strength and stiffness but gave compounds that were less tough.
- Two-way Analysis of Variance (ANOVA) indicated significant polymer-wax interactions.

The urea content determined the stiffness (elastic modulus) of the compounds. PVOH mouldings had superior stiffness compared with the EVA and cooked urea-based mouldings. The Dynamic mechanical analysis (DMA) results confirmed the result obtained from the modulus of elasticity determination in the three-point bending test.

The impact strength increased with an increase in polymer content and reduced with an increase in wax content.

The linear thermal expansion coefficient decreased as the urea content was increased. Measured values (100 to 156x10⁻⁶ °C) were comparable to those of the benchmark.

The cooked urea-based moulding compound had the lowest melt viscosity at 110°C, as indicated by its melt flow index (MFI). Fluidity increased with the polymer content.

The thermo gravimetric analysis (TGA) results confirmed that both the PVOH and EVA urea-based moulding compounds decomposed readily and left less than 1 wt % ash after combustion.

From the SEM results apparent surface roughness appeared to increase with wax content. The EVA urea-based moulding compound had an irregular surface texture.

Based on the criteria of cost-effectiveness and environmental friendliness, the synthesis of PVOH urea-based patterns is preferable. The use of a conventional extrusion process to prepare PVOH urea-based patterns is recommended.

Keywords:

Urea, wax, ethylene vinyl acetate, polyvinyl alcohol, non-biodegradable pattern, biodegradable pattern, investment casting

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LIST OF ABBREVIATIONS

ANOVA	=	Analysis of variance
DMA	=	dynamic mechanical analysis
DMF	=	dimethyl formamide
DSC	=	differential scanning calorimeter
EVA	=	ethylene vinyl acetate
MFI	=	melt flow index
PEG	=	polyethylene glycol
PET	=	polyethylene terephthalate
PVC	=	polyvinyl chloride
PVOH	=	polyvinyl alcohol
phr	=	parts per hundred of resin
SEM	=	scanning electron microscope
SDTA	=	Scanning differential thermal analysis
TGA	=	thermogravimetric analysis
TMA	=	thermomechanical analysis
UE	=	EVA urea-based moulding compound
UF	=	resin
UP8	=	PVOH urea-based moulding compound of plasticisation degree 80
UP4	=	PVOH urea-based moulding compound of plasticisation degree 40
VA	=	vinyl acetate
X: Y: Z	=	proportion of urea: polymer: wax

LIST OF SYMBOLS

A	=	weight of the sample in air (g)
B	=	weight of the sample immersed in water (g)
B	=	width of beam tested (mm)
c	=	volumetric fraction of polymer
D	=	maximum deflection of the centre of the beam
D	=	depth of beam tested (mm)
E	=	modulus
E_B	=	Young's modulus of bending
ε	=	strain at time t
ε_0	=	strain at a maximum strain
F_Z	=	force in the Z direction
H	=	height
L	=	liquid phase
L_S	=	support span
L_1	=	length at T_1
L_2	=	length at T_2
M	=	measured torque
M_D	=	maximum deflection
M_L	=	maximum load
n	=	number of components in the blend
ρ_s	=	density of the sample (g/cm^3)
ρ_L	=	density of liquid (g/cm^3)
ρ_C	=	density of the moulding compound
ρ_i	=	density of the component
w_j	=	weight fraction of component
r	=	radii of the particles
R	=	cone radius
S	=	solid phase
T	=	time
ΔT	=	change in temperature

m	=	steepest load deflection curve slope
T_{om}	=	onset melting temperature
T_c	=	crystallisation temperature
T_{oc}	=	onset crystallisation temperature
T_g	=	glass transition temperature
T_{g1}	=	glass transition temperature of the polymer
T_{g2}	=	glass transition temperature of the plasticizer
U	=	velocity
V	=	vapour phase
V_1	=	free volume
V_o	=	occupied volume
W_D	=	work done
w_1	=	weight fraction of the polymer
w_2	=	weight fraction of the plasticizer
ω	=	frequency of oscillation
w_i	=	weight fraction of component
γ	=	surface tension
α	=	coefficient of linear thermal expansion
Ω	=	rotational velocity
Φ	=	angular displacement; $\beta = \theta - x/2$ (typically 2° - 8°)
θ	=	cone angle
σ	=	stress at time t
σ_0	=	maximum stress
η	=	viscosity
η_e	=	elongation flow
η_s	=	shear flow
$\dot{\gamma}$	=	shear rate

CHAPTER 1 INTRODUCTION

Metals are essential industrial materials due to their good mechanical properties. Metals combine properties of high strength with the ability to change shape without brittle fracture compared with wood, plastics and stone. This enables metals to be formed into a wide range of shapes. Metals are normally extracted from ores and are prepared using various metal-forming processes such as casting, forging and extrusion. Casting involves the pouring of molten metal into a mould or a die. After cooling, the metal takes the shape of the mould and can then be used to form metal components. Common examples of casting processes include sand, dies, centrifugal casting, full moulds, squeeze, investment casting, etc. Alternatively, forging can be used to form metal components. Forging involves forming a metal by heating it in a forge and beating or hammering it into the required shape.

Investment casting is accepted as the most versatile, flexible process in that it produces “near net-shape” metal components compared with other metal-forming processes. Near net-shape provides metal components that are accurate in dimension and surface structure and thus this reduces the amount of waste material in metal casting produced during finishing step compared with other types of metal forming process.

The investment casting process normally involves a disposable wax pattern by injecting wax into a metal die, building a ceramic shell mould by dipping the wax pattern into a slurry, dewaxing the mould and casting the molten metal into the resultant cavity.

Traditionally, urea-based investment casting moulding compounds are synthesised using a cooking process. Nowadays, industries use fast processes, such as conventional extrusion processes, to increase the rate of throughput. The commercial cost performance ratio is another important aspect to be considered. Since waxes are expensive and do not have good mechanical properties, effort is being focused on maximising the filler content and concurrently maintaining the following requirements for quality control needed by an investment caster:

- The pattern must not change shape (creep) during storage/handling
- The pattern must not break during the handling, assembly and storage steps.
- The pattern must not react with the refractory mould.
- The pattern must burn out of the refractory mould leaving an ash content of 0,014 wt % or less.

- The pattern must not shrink or distort in order to produce accurate dimensional stability close to the accepted tolerance.
- It must be possible to produce the pattern at minimal lead times using conventional extrusion methods.
- It must be possible to produce the pattern cost-effectively.
- The pattern must not emit carcinogenic material in order to be environmentally friendly.
- The pattern should have a good surface finish.

Urea is a highly crystalline organic compound commercially available in prill form. It is inexpensive but it degrades just above its melting point of ca. 134°C to produce ammonia and carbon dioxide and therefore cannot be processed using conventional extrusion processes.

Polyvinyl alcohol (PVOH) is an attractive biodegradable polymer used in different areas of science and technology, especially in adhesives for paper, wood, textiles, food and pharmaceuticals. It offers flexibility, transparency and toughness compared with other barrier polymers. However, the melting point of the crystallites of PVOH is above the thermal degradation temperature which is ca. 170°C. For this reason plasticisation technology using glycerol is employed to lower the melting point of polyvinyl alcohol to just below the melting point of urea. This improves the processability of both urea and PVOH, and also eliminates the required slow cooking process if the conventional extrusion process is employed. However, plasticisation is a time-consuming process and because urea is very soluble in water, it cannot be pelletised directly using water.

The use of a hot-melt adhesive such as ethylene vinyl acetate (EVA) is highly advisable since it offers good adhesion to a variety of materials and it is not expensive. Also, EVA offers a wide range of high-melt flow indices and low melting temperatures. Because of its low melting temperature and its good compatibility with wax, EVA can be compounded with urea below its melting point.

Low cost, high lubricity and low melting viscosity are the main properties that make wax a valuable organic pattern material in investment casting.

The present study considered the following important aspects of urea-based moulding compounds for investment casting:

- The optimisation of the formulation with regard to the content of urea, PVOH, EVA and wax
- The development of novel compounding techniques to be used to synthesise EVA urea-based and PVOH urea-based moulding compounds for investment casting.
- Characterisation of the moulding compounds to meet the requirements of investment casters by comparing them with a characterised industrial cooked urea-based moulding compound.

The study is, however, limited in that urea/PVOH moulding compounds were produced using a two-roll mill only. The use of conventional extrusion processes was not investigated.

CHAPTER 2 INVESTMENT CASTING

2.1 History of investment casting

Investment casting originated several thousand years ago: Ancient Egyptian and Chinese museum pieces suggest that they were made by investment casting processes (Little, 1977). According to Black, *et al.* (1984), "Dentists have also used the process since the turn of the century". It did not, however come into common industrial use until World War II (1939-1945) when high-quality jet turbine blades and supercharger buckets for aircraft engines were in great demand.

2.2 Investment casting process

Figure 1 illustrates the current industrial investment casting process. It starts with the manufacture of a pattern using an injection moulder or a wax injector. The patterns are attached to a common sprue and then invested, i.e. "dipped", in slurry to create a thin coating on the surface. Dipping in a refractory slurry mixture is repeated until a coat of the correct dimension is achieved and finally a granulated refractory 'stucco' shell is applied (Repp, 1994). The pattern-sprue system is then conditioned and left to dry.

The coated cluster is then placed in a boilerclave where the pattern melts (de-waxing) and runs out through the gates, runners and pouring cup. The ceramic shell moulds are fired in a furnace to form the final mould walls. In the process, leftovers of the wax burn out. The hot moulds are filled with molten metal and allowed to cool. After the moulds have cooled, the ceramic material is removed from the casting cluster by either mechanical or chemicals means. Finally, the individual castings are removed, machined and polished. Figure 1 depicts the entire process of investment casting.

Advantages of investment casting

- Precision, flexibility, reliability and good surface finish is there in investment casting compared with other metal-forming processes.
- There is no requirement to make draft angles to give any accuracy or versatility needed.

- The investment casting process is also versatile in that a wide range of materials can be formed and cannot be formed by any other metal forming process.
- Because of the high degree of dimensional accuracy and the excellent surface finish, little or no machining is required, leading to savings on raw material.

Disadvantages of investment casting

- The size of parts is limited because it becomes difficult to form moulds for large objects.
- The machinery and dies are expensive.
- The unit cost is high and the process is labour-intensive.

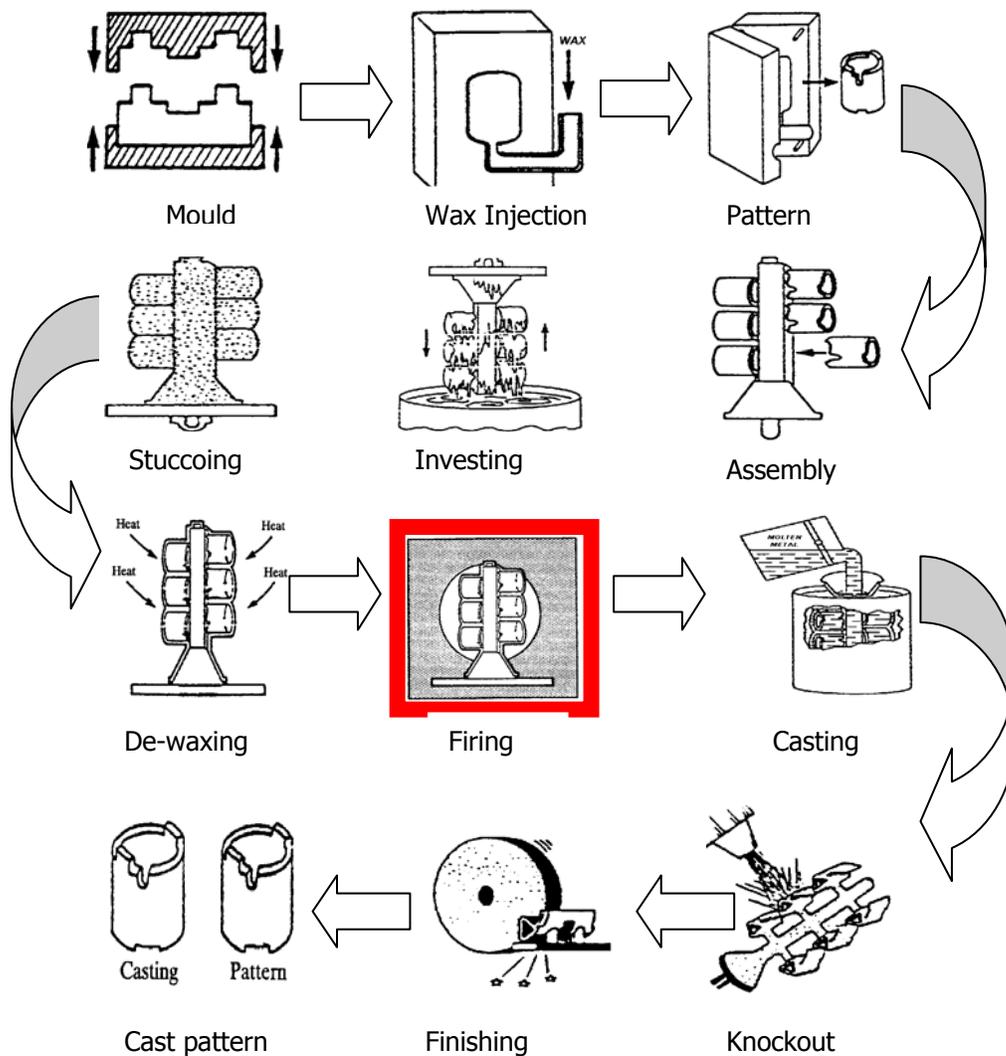


Figure 1: Investment casting process (Biam, 2004)

CHAPTER 3 MOULDING COMPOUNDS FOR INVESTMENT CASTING

3.1 Wax based moulding compounds for investment casting

Fillers, additives, resin, paraffin and microcrystalline waxes are typical ingredients used to formulate wax-based moulding compounds for investment casting. There are basically five types of wax based moulding compounds for investment casting, as discussed below (Rajesh, 2004).

1) Straight or unfilled moulding compound

Straight or unfilled investment casting pattern waxes are waxes that do not contain any filler. These waxes can be recycled and reconditioned easily in contrast to other investment casting waxes. Straight patterns are more expensive than filled moulding compounds (Rajesh, 2004). They are mainly used for runners.

2) Filled moulding compound

Filled patterns contain fillers to extend the primary waxes. The inclusion of low-cost fillers reduces the cost of the compound but, more importantly, they reduce the linear thermal expansion coefficient of waxes. This reduces surface defects, such as sinks and cavitations.

3) Emulsified “fillers”

This type of pattern utilises water as a “filler material”. Pattern wax containing emulsified water reduces the cost even further as it eliminates the use of solid fillers. Also they are easily removed from ceramic shell in the de-waxing process without cracking of the shell.

4) Adhesive waxes for the assembly of wax patterns

Adhesive waxes are used to assemble patterns for the main sprues. They are generally of high strength to hold the weight of heavy assemblies.

5) Patching and repair waxes

These wax moulding compounds are used to repair defects such as flow lines, sink marks and holes due to air entrapment.

3.3 Other moulding compounds for investment casting

1) Mercury pattern compounds (Mer casting, 2006)

In this case frozen mercury is used as a pattern material instead of wax. Liquid mercury is poured into a mould where it freezes at low temperatures. Then it is removed and coated with cold refractory slurry to the required thickness. The refractory shell is dried at low temperature the shell and mercury are brought to room temperature and the mercury is melted out. Complex parts can be made using mercury. Very close tolerances and excellent surface finish can be obtained but it is a very expensive method.

2) Ice pattern compounds (Zhang, 1999)

The Rapid Freezing Forming (RIF) is similar to the Melt Extrusion Modelling (MEM). It uses pure water as a pattern material. At low temperature, water is sprayed through a nozzle to a selected place under the computer's precise control, and is frozen rapidly. The solid part is built from the bottom up to the top layer-by-layer. Advantages of using ice patterns include: High precision (because ice pattern shrinks on melting, i.e. it does not expand like wax patterns), low cost and the environmentally friendly nature of water.

3.3 Principles of compound formulation

Fillers, additives, resin, paraffin waxes and microcrystalline waxes are the ingredients used to process wax based investment casting moulding patterns. Examples of wax moulding compounds include:

Polyethylene terephthalate investment casting moulding compounds

Guinn (2002) invented a wax pattern containing up to 50 wt % polyethylene terephthalate (PET) powder. The use of PET as a filler reduces the thermal contraction and expansion properties of wax, increasing the degree of dimensional accuracy. PET is relatively cheap compared with other inert fillers, can be easily removed from the mould without any form of shell cracking, produces extremely low ash when burned and is compatible with fillers such as organic acids, cellulose acetate, urea, bisphenols, polyacrylates, polystyrene and other high-melting-point polyols. It also has a higher specific gravity that ranges between 1.31 and 1.45 g/cm³, which allows it to be separated from the base wax for reclamation. The PET formulation used in the research is shown in Table 1.

Table 1: Formulation of an investment casting compounding containing polyethylene terephthalate (PET) as filler (Guinn, 2002)

Compound	Mass %
Paraffin wax	14
Microcrystalline wax	7
Candelilla wax	4
Aliphatic C5 hydrocarbon resin	10
Polyterpene resin	23
Polyethylene resin	2
Polyethylene terephthalate	40

Urea based investment casting moulding compounds

Fujita (1990) synthesised a urea pattern moulding compound based on a PVOH binder together with eutectic formers. The latter ingredient purportedly improves the processability of the

compound by reducing the melting point of urea. Typical formulations contain up to 95% urea. Fujita (1990) claims that urea forms a eutectic mixture with the following substances: benzoic acid, benzene sulphonic chloride, barium salt, benzoyl chloride, glycine, naphthalene and glutaric acid. According to Fujita (1990), good results are obtained when the polymer contains 1 – 8 wt % benzoic acids. The advantage of this invention is that the pattern (compound) can be injection-moulded at very low pressure, minimising tooling cost and producing a pattern with an excellent surface finish and a close dimensional stability.

Urea patterns are easily removed by melting from the ceramic shell moulds. Since urea is water-soluble, it can also be removed using steam. However, the water-solubility implies that urea easily leaches out of a wax formulation as a result of humidity or contact with water from slurries. Another disadvantage is that urea degrades easily and therefore it presents processing problems.

Urea is also used as a filler in wax investment casting patterns (Horton, 1988). It reduces the linear thermal coefficient of expansion and increases the stiffness of wax in investment casting patterns, leading to the accurate dimensional stability of patterns (Guinn, 2002). Urea is water-soluble and can therefore be easily removed from moulds using steam. However, its water solubility and hygroscopic nature increase the chances of urea leaching out of the wax formulation under ambient conditions or by water from slurries.

Sturgis *et al.* (2001) proposed polycarbonate binders (at 10% to about 50% by mass) to reduce the thermal expansion coefficient of wax patterns.

3.4 Fillers

Fillers are solid granular materials that can be dispersed into a polymer matrix, without affecting the molecular structure of the polymer. Fillers are used to improve the mechanical properties of polymers. They are low in cost and can be used at high volume loadings to provide economical compounds (Gächter & Müller, 1984). Table 2 summarises the important properties that make fillers useful in the plastics industry.

Table 2: Useful properties of fillers in polymers (Gächter & Müller, 1984)

Properties	Advantage
Mechanical and physical	Fillers increase hardness, impact strength and density; they improve surface quality and dimensional stability.
Thermal	Fillers reduce the linear coefficient of thermal expansion and the contraction of compounds. Fillers offer high heat-deflection temperature, high resistance to thermal shock, and good flame and glow resistances.
Chemical	Fillers offer good chemical resistance, weather resistance properties, and low water absorption.
Electrical	Generally, they significantly increase the porosity, reduce the dielectric strength, and lower the dielectric constant and dissipation factor.
Tribological	Wear rate is reduced.
Economic cost	Fillers are cheap and therefore offer low cost per unit volume of a material.

Fillers materials are usually inert and act as a bulking agent (Felder, 1995). Investment casting fillers are either ceramic in nature or are amorphous polymers that feature low coefficients of thermal expansion. Waxes undergo a large volume change when they melt or crystallise. This is highly undesirable when precision moulds are required. Since fillers do not melt, they tend to ameliorate the solidification shrinkage effect of the wax.

Fillers that have been used in pattern waxes include various dicarboxamides and related compounds, isophthalic acid, pentaerythritol, hexamethylenetetramine, urea, terephthalic acid, PET, water, and normal and cross-linked polystyrene or methyl methacrylate. Good fillers in investment casting waxes should:

- Be inert to the base wax and thermally stable.
- Be spherical and have a small particle size to ensure a smooth surface finish.
- Have a minimal ash content to minimise the formation of undesirable material during the dewaxing and firing process.

- Have a specific gravity similar to that of the wax pattern to minimise settlement.
- Have a good surface finish when injection-moulded.
- Be environmentally and user-friendly.
- Be inexpensive.

3.4 Urea

Urea is produced commercially. Because it is highly hygroscopic, it is sold commercially in prill form to avoid caking and for make it easy to handle (Anon, 1993). The main properties that make urea an important organic compound in industrial applications are listed in Table 3.

Table 3: Crucial properties of urea (Anon, 1993)

Property	Advantages
Chemical	Forms an inclusion compound and eutectics; is fully soluble in water and partially soluble in alcohol.
Thermal	Reduces the linear thermal coefficient of thermal expansion, contraction of compounds and thermal conductivity.
Mechanical	Has good dimensional stability; increases hardness and reduces creep.
Electrical	Increases porosity, reduces the dielectric strength and raises the dielectric constant and dissipation factor.
Economic	Is one of the cheapest fillers in the world
Environmental	Is biodegradable and produces no carcinogenic material.

3.4.1 Applications of urea

Urea ($\text{CO}(\text{NH}_2)_2$) is mostly used in agriculture as a fertiliser. Statistical data from 29 urea-manufacturing plants in the United States show that 85% of urea was used as fertilisers, 3% in animal feed and the remaining 12% in plastics and in other uses (Anon, 1993).

Pharmaceutical applications

Urea and malonic acid react to form barbituric acid. Urea is also used in the production of various acylureas and urethanes for use as sedatives and hypnotics.

Applications in resins

Melamine is formed by the dehydration of urea. Melamine is used primarily in the production of melamine-formaldehyde resins for laminates, moulding compounds, coatings and textile finishes (Meyer, 1979).

The manufacture of UF resins involves the reaction of formaldehyde with urea under controlled conditions. Adhesives based on formaldehyde are used as binders in the production of reconstituted wood panels, such as particleboard, plywood, medium-density fibreboard, laminated veneer lumber, finger joints and laminated beams. UF resins and other related formaldehyde resins are also used in resin-impregnated decorative paper laminates, fibreglass insulation binders, foundry cores, pulp and paper processing aids, paper sizing, textile treatments, paints and enamels, and miscellaneous joinery applications (Anon, 1993).

Agricultural applications

In fertilisers, urea is used as a nitrogen-releasing agent since it hydrolyses to form 2NH_3 and CO_2 .

3.4.2 Physical and thermal properties of urea

Urea has definite advantages as a primary moulding material. It has a low coefficient of thermal expansion. The volume of the melt is lower than that of the solid near the melting point (Meesen & Petersen, 1986). This facilitates the removal of the pattern from the shell without causing it to crack (see Figure 2). Urea is water soluble and a crystalline solid.

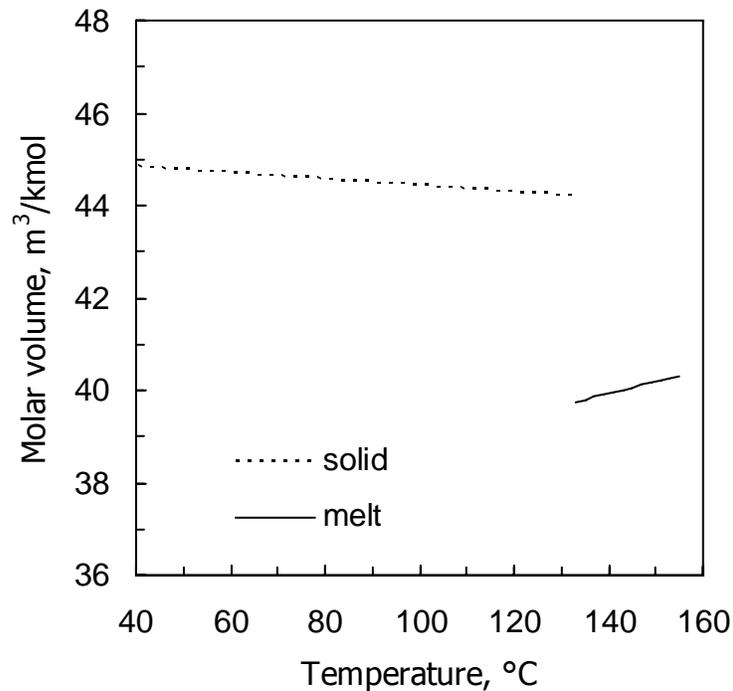


Figure 2: Molar volume of urea as a function of temperature (adapted from Meesen & Petersen, 1986)

Urea eutectics (Sekiguchi & Obi, 1961)

Although urea has highly desirable thermo-volumetric properties, it unfortunately starts to decompose at temperatures just above its melting point. Fortunately, the addition of a third component will cause a reduction in the melting point, the so-called "freezing point depression" or "eutectic formation" phenomena. Simple eutectics are based on binary mixtures that have negligible solid–solid solubility but in which the liquids show complete miscibility. Thermodynamically, the solids system is an intimately blended physical mixture of its two crystalline components.

Urea forms eutectic mixtures with methyl urea, dimethyl urea, acetamide, benzoic acid, etc. For example, when urea and acetamide are mixed, heated and cooled at different compositions, a eutectic composition with a minimum freezing point is formed as urea and acetamide crystallise simultaneously (Sekiguchi & Obi, 1961). Figure 3 below depicts the phase diagram of the urea-acetamide system as determined in this study.

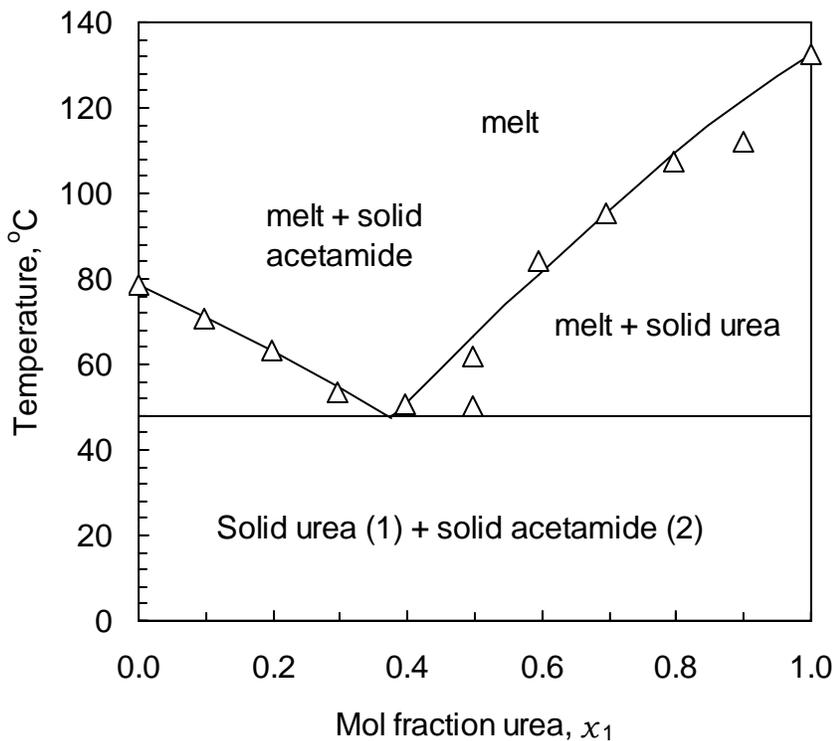


Figure 3: Phase diagram for the urea (1) – acetamide (2) system (Walbrug, 2006)

Urea inclusion compounds

Urea forms clathrates, i.e. inclusion compounds with straight-chain hydrocarbons. The urea crystal host structure consists of extensively hydrogen-bonded arrangements of urea molecules. They are arranged such that they form parallel, one-dimensional tunnels. The distance between the centres of adjacent tunnels is ca. 8.2 Å.

The tunnels are filled with a dense packing of guest molecules to make the host structure stable. The diameters of these tunnels are ca. 5.5 – 5.8 Å. The guest molecules must be sufficiently long, with a limited degree of substitution (Sang-Ok & Harris, 1999).

The formation of urea inclusion compounds involves the growing of crystals and a recovery mechanism. A typical preparation procedure for inclusion compounds involving urea (the "host")

and the "guest" is as follows: Both are separately dissolved to form saturated solutions in methanol at 55°C. The combined solution is warmed and continuously stirred. A white precipitate is obtained over the period of a day; it is further filtered and washed with warm toluene (Sang-Ok & Harris, 1999).

3.5 Polymers

Polymers are composed of long molecule carbon and hydrogen based chains. Polymer morphology refers to the structural form (packing) adopted by its collection of molecule chains. Polymers can be classified as being either *amorphous* or in a *semi-crystalline state*. The molecules of completely amorphous polymers exhibit an irregular microstructure. Crystalline polymers have sufficient molecules to form regular structures (organisation of atoms along the chain).

The molecular motions that do occur in amorphous polymers determine the *glass transition temperature*. These motions include the conversion of entire molecules, "wriggling" and "jumping" of segments of molecules, the movement of atoms in the main chain or in side-groups on the main chain, and the vibration of atoms about the region of equilibrium (Rodriquez, 1989).

The glass transition temperature (T_g) is the temperature at which the polymer begins to exhibit long-range, co-operative segmental motion. Below T_g , amorphous polymer chains are effectively frozen and cannot flow under applied stress; the type of motion is also restricted to vibration modes. Thus the material is hard and glassy. Above T_g , there is enough thermal energy for the chains, through co-operative rotation, to flow under applied stress. The company of large-scale segmental motion above T_g produces an increase in the free volume. *Free volume* is the difference between the actual and occupied volumes of a polymer (Sperling, 1992). The free volume can be described as the "space" that is available to polymer chains. An increase in the free volume of a polymer results to an increase in the "space". This provides more mobility and thus produces a less rigid and more flexible polymer. A graph of polymer free volume vs. temperature is shown in Figure 4. The graph shows that the free volume is constant below T_g

but increases with temperature above T_g . For all polymers, the ratio of free volume to total volume is about 0.05 at T_g .

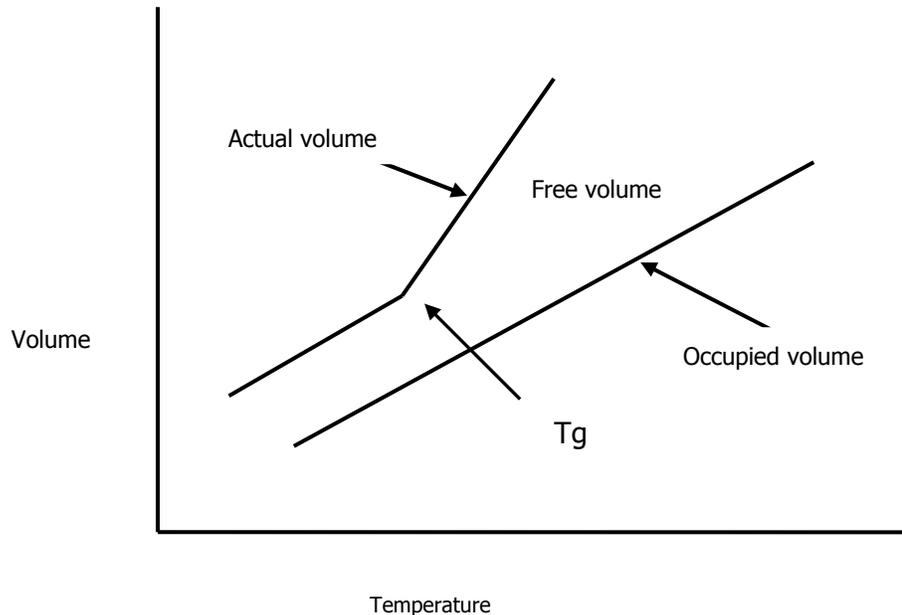


Figure 4: Polymer volume versus temperature (Sperling, 1992)

Polymers offer flexibility, high resistance to rupture and excellent adhesion to a wide range of substrates. The most common types of resins used in investment casting include polyethylene, ethyl cellulose, nylon, polyvinyl alcohol, ethylene vinyl acetate and vinyl acrylate (Horton, 1988).

3.5.1 Ethylene vinyl acetate

Ethylene vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate. The vinyl acetate groups are distributed randomly along the long polymer chains (Elvax, 2004). Different EVA grades are distinguished on the basis of their vinyl acetate (VA) content and their melt flow index (MFI). The latter property relates back to the molar mass of the polymer. The physical and mechanical properties of selected EVA grades are shown in Table A4 in Appendix A.

EVA copolymers are commercially available at VA contents ranging from 18 - 40% VA and 0.4 - 500 MFI. EVA polymers are applied in adhesives, sealants, wax bends, hoses and tubing, wire and cable insulation. EVA is the third major class of hot-melt adhesives used in industrial applications (Elvax, 2004).

Physical and chemical properties of EVA

EVA resins soften gradually and continuously with increasing temperature and do not exhibit much solid-to-liquid expansion during heating or contraction during cooling. In summary, resins are used to offer the following important properties (Elvax, 2004):

- Flexibility
- High cohesive strength and compatibility
- Excellent adhesion to a wide range of substrates
- High resistance to rupture
- Lower coefficient of thermal expansion.

Compatibility of EVA and paraffin wax

EVA resin is compatible with wax because it also contains long sequences of $-\text{CH}_2-$ units that are linked together. If its crystallisation temperatures overlap with that of the wax, co-crystallisation occurs, with these sequences being incorporated into the wax crystals. This co-crystallisation process allows the EVA resin to reinforce the wax, making a compatible blend. Such blends show significant improvements with respect to mechanical properties such as toughness. EVA resins with 18 to 28 wt % vinyl acetate content melt at 70 - 87°C and freeze at 66°C. This range overlaps with that for paraffin waxes. This is the reason why the paraffin waxes were chosen as candidate lubricants in this study.

At VA content levels greater than 28 wt %, EVA and wax become less compatible due to changes in the freezing point but also because there will be fewer long $-\text{CH}_2-$ sequences. Vinyl acetate sequences are not incorporated into wax crystals.

Figure 5 shows the compatibility relationship between vinyl acetate content and wax using the cloud and freezing point. Cloud point is the temperature where the first crystallites start to

form. The cloud and freezing point were measured for blends of 10% EVA and paraffin wax at different VA contents, using a differential scanning calorimeter (Elvax, 2004)

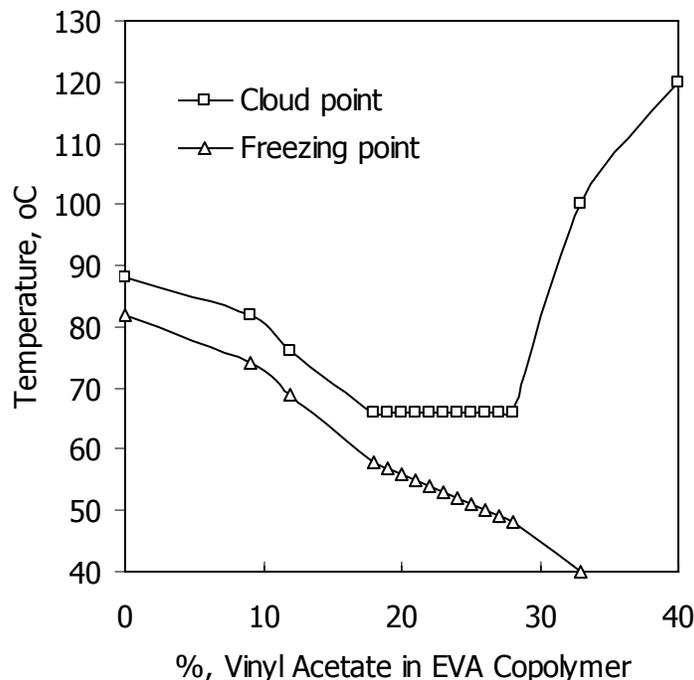


Figure 5: Cloud and freezing point for 10% EVA, with different VA contents, dissolved in paraffin wax (Elvax, 2004)

3.5.2 Polyvinyl alcohol

Polyvinyl alcohol (PVOH) is a water-soluble resin produced by hydrolysing polyvinyl acetate. PVOH products are divided into two main groups, namely full hydrolysed and partially hydrolysed. The two groups differ in their physical properties, as shown Table A2 in Appendix A. Commercially, PVOH is available in the form of white granules. The properties that make PVOH useful in industrial applications are given Table 4.

PVOH offers a combination of excellent film-forming and bonding characteristics. This makes it useful in a variety of applications. Examples of PVOH adhesives applications include: paper and paperboard sizing and coating, textiles, building products and ceramic processing.

The melting point of PVOH is above the thermal degradation temperature. Therefore PVOH has to be plasticised to improve its processability.

Table 4: Physical properties of polyvinyl alcohol (Finch, 1992)

Property	Advantages
Chemical	Chemically soluble in hot water, but insoluble in cold water.
Permeability	High degree of impermeability to gases; forms a coating that provides excellent barrier properties.
Mechanical	High tensile strength; forms a tough, abrasion and tear-resistant film if plasticised. Good adhesive properties.
Optical	Practically opaque.
Moulding	Can be extruded and compression-moulded if plasticised.
Oil and solvent resistance	Resistant to animal and vegetable oils, greases and petroleum hydrocarbons.
Other	Biodegradable, environmentally friendly.

3.6 Plasticisers

A plasticiser is a material of low molecular weight added to polymeric materials such as paints, plastics or adhesives to improve their flexibility and lower their glass transition temperature (T_g). Plasticisers interact with polymer chains on the molecular level to increase chain mobility and to speed up the viscoelastic response (George, 2004).

Plasticisers are commonly classified according to the chemical family to which they belong. Polyvinyl chloride (PVC) is the polymer most often plasticised. PVC plasticisers include esters, phthalates and chlorinated paraffin.

3.6.1 Glycerol

Glycerol is a good plasticiser for polyhydric polymers such as PVOH. Glycerol is an alcohol with a three-hydroxyl group in its chemical structure. It is a clear water-white, hygroscopic, colourless,

odourless, non-toxic and non-irritant liquid (George, 2004). The physical and chemical properties of glycerol are listed in Table A5 in Appendix A.

Glycerol is obtained from glycerides during the process of soap manufacture and fatty acid production. Fat is reacted with caustic soda solution to form soap and glycerol. Glycerol is available in liquid form and should be stored in waterproof containers due to its hygroscopicity.

Glycerol and its esters are used mainly in cosmetics and toiletries, pharmaceuticals, food and beverages, industrial plasticisation of polymers, etc. The beneficial properties that make glycerol useful in industrial applications are given in Table 5.

Table 5: Industrial beneficial properties of glycerol (George, 2004)

Property	Advantages
Rheological	Modifies the flow properties of polymers.
Mechanical	Improves ductility and improves impact resistance. Increases elongation and lowers the tensile strength.
Optical	Improves optical clarity.
Processability	Lowers fusion, gelation and melting temperature, and this improves material processing ability (lowers the degradation rate).
Permeability	Improves gas permeability.
Biological attack	Increases biodegradability attack.
Compatibility	Improves compatibility between polymers with additives.
Solubility	Completely soluble in water and alcohol; insoluble in hydrocarbons.

3.6.2 Mechanism of plasticisation

The first theory of plasticisation was developed between 1930 and 1940 (George, 2004). There are two classical theories explaining the plasticisation of polymers, namely the *gel theory* and the *lubricity theory* (Kirkpatrick, 1940). The free volume theory was developed later between 1948 and 1958.

Lubricity theory (Kirkpatrick and Houwink, 1940)

Kirkpatrick and Houwink (1940) developed the lubricity theory of plasticisation. The lubricity theory states that the role of a plasticiser is to reduce the intermolecular friction between polymer molecules, so that the molecules can slip and slide over each other.

The gel theory (Aiken, 1947)

The gel theory supposes that the polymer structure forms a three-dimensional “honeycomb” structure. It states that the polymer's rigidity can be attributed to this three-dimensional network. The plasticiser reduces the polymer-polymer union and thus reduces the rigidity of the polymers. There is a dynamic equilibrium involving solvation-desolvation of the polymer by the plasticiser and aggregation-desegregation of the polymer chains themselves. Thus the success of the plasticiser depends on the strength of attraction involved and on the mobility of plasticiser's molecules.

Free volume theory (Fox and Flory, 1948; Ueberreiter and Kanig, 1952)

After the lubricity and gel theories, the free volume theory emerged from the evolution of different properties of polymers as a function of temperature, specific volume, coefficient of thermal expansion or viscosity. This theory, postulated by Fox and Flory, further explains some properties of plasticised polymers. According to Fox *et al.* (1948), the viscosity at any glass transition temperature is approximately 10^{12} Pa.s, independent of the polymer's chemical structure. The free volume theory considers the available space or “free volume” between the molecules. At high temperatures this free volume is large. Fox and Flory defined the free volume at temperatures above the glass transition temperature. The free volume at all temperatures should be zero for all kinds of glasses. Kanig suggested that free volume is the difference between the volume measured for the crystals and the volume observed at zero temperature, glass or liquid, for a given use (Ueberreiter, 1952).

It is not easy to measure specific volume at absolute zero temperature and therefore this makes the theory behind free volume somewhat vague. Above T_g the segments are so densely packed that internal mobility is negligible.

Some models were developed to correlate the free volume fraction with T_g for polymers. These are discussed below.

Mathematical model

A series of mathematical models based on the free volume theory were formulated. These models allow the prediction of the effect of blending polymers with each other, or of adding a plasticiser to a polymer (Wood, 1958):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

Where T_g , T_{g1} and T_{g2} are the glass transition temperatures in Kelvin of the compound, polymer and plasticiser respectively, and w_1 and w_2 are the mass fractions of the polymer and plasticiser respectively. Plasticiser efficiency can be quantified by the extent to which a plasticiser reduces the T_g of the polymer (Gordon & Taylor, 1952).

Kelly & Bueche (1961) and Couchman (1963) revised the Gordon and Taylor model by considering the effect of thermal expansion on T_g . The latter authors derived the following equation:

$$\ln T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{\Delta C_{p1} T_{g1} + \Delta C_{p2} T_{g2}} \quad (2)$$

where the symbols have the same meaning as for equation (1) and ΔC_p is the increment of heat capacity of the pure components at their respective T_g 's in °C.

Gibbs-DiMarzio theory

The Gibbs-DiMarzio theory assumes that the experimental glass transition is a kinetic manifestation of an underlying, thermodynamic, second-order phase transition. This theory provides a framework for predicting the effect of variables such as molar mass, plasticiser content, cross-link density and mechanical deformation on T_g (Mark *et al*, 2004).

3.6.3 Factors influencing plasticisation

Plasticisation occurs only as a result of an increase in free volume which permits an increase in the motion of a polymer's molecules. Free volume can be increased from three sources, namely:

- The motion of the chain ends
- The presence of a side chain
- The motion of the main chain.

Increasing the above-mentioned motions can increase free volume by:

- Increasing the number of end-groups by lowering the molecular mass
- Increasing the number or length of the side chain
- Increasing the chain movement by including segments of low steric hindrance and low molecular attraction
- Addition of a compatible compound with a lower molecular weight
- Increasing the temperature.

Thermal properties of plasticised polyvinyl alcohol blends

Jang *et al.* (2003) studied the plasticizer effect on the melting and crystallisation behaviour of PVOH. A blend of glycerine and PVOH granules was dried in a vacuum oven at 80 °C for 1 h. The PVOH-glycerol mixture was then extruded using a Plasticorder single-screw extruder (L/D =25) at 210 °C. The thermal properties were characterised using a DSC from 30 to 250 °C at a heating and cooling of 20 °C per minute. Jang *et al.* (2003) found that the melting temperature decreased with increasing amount of glycerine. This suggests that an increase in the amount of glycerine increases the segmental mobility of PVOH chains and reduces the crystallinity of the polymer. Figure 6 below shows the effect of increasing the glycerine content on the melting point of partially hydrolysed PVOH.

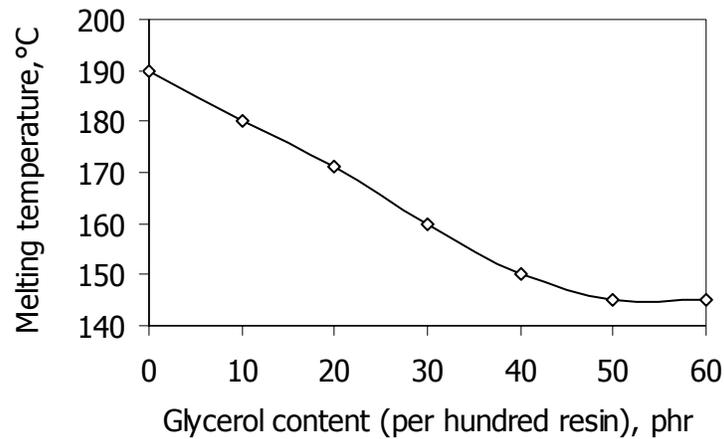


Figure 6: Effect of glycerol on the DSC melting peak temperature of partially hydrolysed PVOH (Jang *et al.*, 2003)

Effect of increasing plasticiser mass on the Young's modulus

Young modulus also known as the modulus gives an indication on the stiffness of a material. It is determined from stress-strain curves. Figure 7 shows that as the mass of plasticiser in the PVC is increased, the Young's modulus decreases.

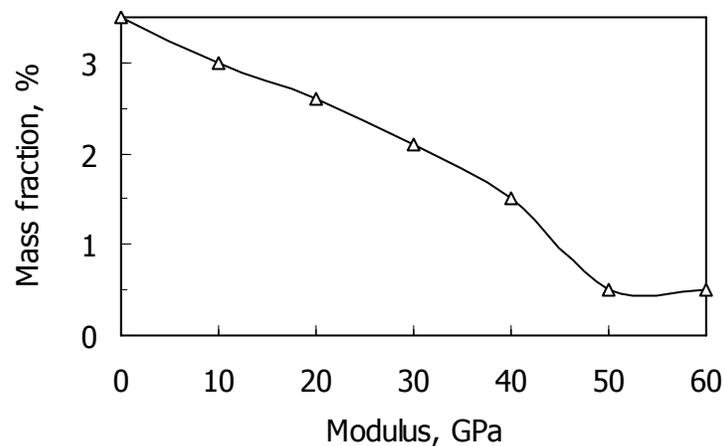


Figure 7: Schematic illustration of the effect of plasticiser addition on the Young's modulus of a polymer

3.7 Lubricants

Lubricants are additives used in polymer processing to modify the rheology of polymer melts. They are divided into external and internal lubricants. The most common lubricants are: synthetic and natural waxes, low-molecular-weight polyethylene, and metallic stearates.

External lubricants are used mainly to eliminate external friction between the polymer and the metal surface of the processing equipment. Internal lubricants improve the internal flow characteristics of a polymer, adding to the wetting properties. Many lubricant systems act as both internal and external lubricants (Hay *et al.*, 2000).

Internal lubricants contribute to the polymer matrix's reduced melt viscosity and improved flow, thereby allowing faster production rates. External lubricants allow the molten polymer mix to flow better at the polymer/processing equipment interface, resulting in better surface appearance and gloss. External lubricants can also contribute to the finished product's "antiblock" and "slip" properties.

From a practical viewpoint, internal lubricants have a high degree of compatibility with the polymeric matrix, whereas external lubricants have a limited degree of compatibility, i.e. they tend to migrate to the surface of the polymer, thereby contributing to a degree of slip between the polymer matrix and the processing equipment surface (Hay *et al.*, 2000).

A number of lubricants have been used in the processing of investment moulding compounds: stearic acid, synthetic wax, beeswax and paraffin waxes (Horton, 1988).

Waxes as lubricants

Waxes are short- to long-chain organic compounds, e.g. hydrocarbons, that crystallise easily. Waxes can be either extracted from beeswax and vegetable raw matter, or manufactured from petroleum feedstocks (Hay *et al.*, 2000).

Types of waxes and their properties

Candelilla and carnauba waxes are extracted from vegetable matter. They have a number of different properties that make them useful in industry. Candelilla wax is moderately hard and slightly tacky with relatively low thermal expansion, i.e. less solidification shrinkage than hydrocarbon waxes. Carnauba has a lower thermal expansion than candelilla wax and is very hard, non-tacky and brittle.

Beeswax has properties similar to those of microcrystalline wax. These types of waxes are, however, subject to supply shortages and are very expensive compared with hydrocarbon waxes (Horton, 1988). There are three main types of waxes manufactured from petroleum feedstocks, namely paraffin, microcrystalline and synthetic wax. The three types differ with respect to their molecular weight, the nature of branching and cost. The differences in the chemical, economic and physical properties of these waxes are presented in Table 6.

Table 6: Chemical, economic and physical properties of hydrocarbon wax (Horton, 1988)

Wax	Chemical, economic and physical properties
Paraffin	Straight-chain hydrocarbon Melting point: 49 -71°C Soluble in benzene and warm alcohol High molecular weight Cost-effective Poor heat resistance
Microcrystalline	Branch-chain hydrocarbon Melting point: 60-89°C Higher molecular weight than paraffin wax More costly than paraffin wax Fair heat resistance
Synthetic wax	Straight-chain hydrocarbon Low molecular weight Higher melting point: 100-110°C Good heat resistance

Application and function of waxes

Commercially, waxes are available in slab and powder form, depending on the application. Low cost, high lubricity and low melt viscosity are the main properties that make wax a valuable organic material in industrial applications (Horton, 1988). Waxes are applied in a number of industrial fields and offer the functions shown in Table 7.

Table 7: Applications and functions of waxes (Horton, 1988)

Application	Functions
Adhesives, hot melts	Viscosity adjuster, lubricants, surface hardening
Building	Bitumen modifier and anti-graffiti treatment
Candles	As a fuel, and for light
Cosmetics	Binders and consistency regulators for ointments, creams, pastes lipsticks, etc.
Electrical and electronics industries	Release agents, insulating materials, etching bases
Medicines and pharmaceuticals	Moulding and release agents in dental laboratories and surface hardening of pills
Plastics	Lubricants, release agent, pigment carriers (master batch)
Investment casting industry	Moulding and release agents in investment casting, surface hardening and strengthening

3.8 Filled polymers

3.8.1 Filler-polymer interaction

The type of filler-polymer interaction determines the mechanical properties of a wax pattern. There are basically three different polymer-filler interactions, namely:

- No interaction between the filler and the polymer. This is the typical situation when the polymer is highly non-polar. In this case, the filler acts merely as an extender and its presence weakens the material.

- The polymer wets the filler surface. This will be the case when the polymer has an affinity for the filler surface. A physical bond will exist between the polymer and the surface of the filler (Shenoy, 1999) and good mechanical properties are possible.
- A true chemical bond forms between the filler and the polymer. This increases the strength of the mechanical properties to an even greater extent (Shenoy, 1999).

3.8.2 Factors affecting polymer-filler interaction

Filler content

Owing to the differences in densities, it is more appropriate to express filler content in terms of volume fractions than on a mass basis. The tensile strength decreases rapidly when the filler content exceeds a critical volume concentration. The presence of filler also increases the melt viscosity of moulding compounds. This can cause processing problems during injection moulding (Bierwagen, 1972).

Wettability

For effective bonding to occur between the filler and the polymer, there should be good wetting. The wetting of a solid by a liquid depends upon the interfacial energies between the solid, liquid and vapour phases. Wetting can be determined using the Young's equation (Zisman, 1963). This relates contact angle measurements. This is shown in Figure 8.

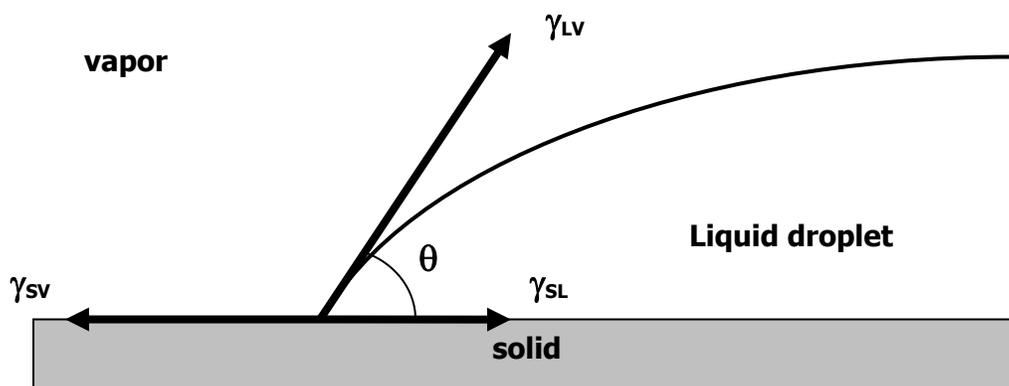


Figure 8: Contact angle when a liquid drops onto a solid surface (Zisman, 1963)

Where γ_{LV} is the liquid-vapour interfacial tension, θ is the contact angle, γ_{SV} is the solid-vapour interfacial tension, and γ_{SL} is the solid-liquid interfacial tension.

The contact angle of a liquid drop onto a flat solid is given by the equation below:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (3)$$

The wettability theory states that for good wetting to occur, the filler (substrate) surface tension γ_{SV} , or its critical surface energy, should be greater than the surface tension of the wetting agent (polymer) (i.e. $\gamma_{filler} > \gamma_{polymer}$). In other words, $\cos \theta = 1$ or θ is equal to 0° .

Filler surface

The micro-configuration and friction of the filler surface play an important role in filler-polymer interaction. Rough filler surfaces offer more adhesion to polymers than smooth fillers, but smooth fillers are more easily wetted than less regular surfaces. Smooth fillers often have undetected absorbed layers of water and contaminant on their surface which affects the degree of adhesion. For perfect wetting to occur there should be no voids in the filler surface (Davis, 1971).

Filler surface treatment

Filler surface treatment is essential to enhance interfacial bonding and thereby the mechanical performance of filled-polymer systems. The surface treatment process involves surface cleaning and the use of modifiers and coupling agents. A coupling agent is a polymeric compound that forms a bond or attaches itself between a polymer matrix and the filler. Coupling agents are added because, in most cases, fillers are not compatible with the polymers (Edward, 2002).

CHAPTER 4 COMPOUNDING TECHNIQUES

The mixing of fillers, wax and resin to produce a desired polymer product is called *compounding*. The polymer and filler are mixed, melted and pelletised for further application. The equipment used for compounding includes single-screw extruders, intermeshing twin-screw extruders, two-roll mills and continuous mixers. A continuous mixer consists of a single-screw extruder for pumping and a short, non-intermeshing, counter-rotating, twin-screw extruder for mixing and melting.

The type of compounding required depends on the type of mixing to be done. Polymers form a matrix or a continuous phase. The additional component forms a dispersed phase embedded into the polymer matrix during mixing. The mixing can occur by three mechanisms, namely distributive, dispersive and molecular interdiffusion (Chung *et al*, 2004).

Distributive mixing increases the interfacial area between the polymer matrix and the dispersed phase. Distributive mixing improves the spatial distribution without cohesive resistance; it is also called "simple or extensive mixing". *Dispersive mixing* reduces the particle sizes of the additional component. For this to occur, the cohesive resistance has to be overcome to achieve finer levels of dispersion. Dispersive mixing is also called "intensive mixing". Generally, dispersive mixing results in distribution. But distribution may also occur without dispersive mixing. Figure 9 depicts distributive and dispersive mixing.

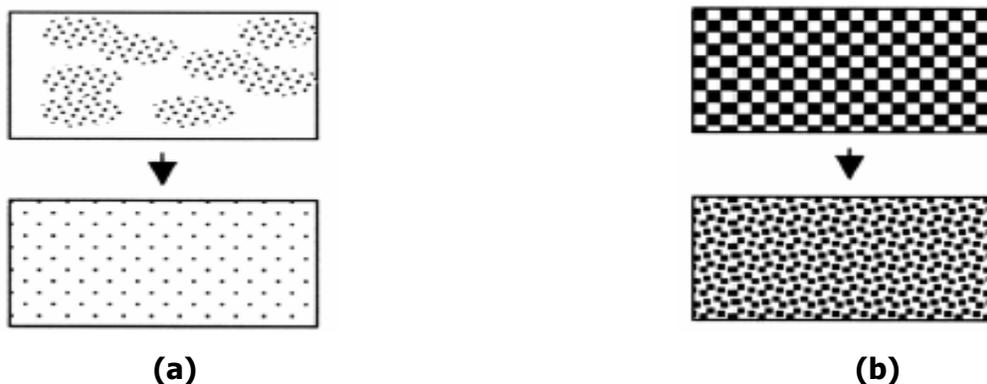


Figure 9: Two types of mixing mechanism: (a) distributive mixing, and (b) dispersive mixing (Chung *et al*, 2004).

If the additional component and the polymer are miscible, molecular interdiffusion occurs in addition to distributive and dispersive mixing. The molecule of the additional component diffuses into the polymer matrix and the polymer diffuses into the dispersed phase. Figure 10 shows the mechanism of molecular interdiffusion.

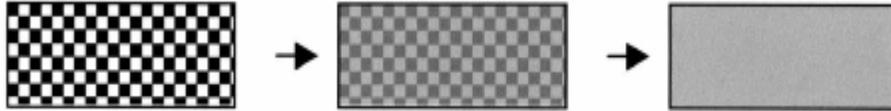


Figure 10: Mixing mechanism: molecular interdiffusion

The molecular interdiffusion increases with an increase in temperature. The time to reach a final composition is inversely proportional to the temperature. At a high temperature, it will take a long time for the polymer matrix and the dispersed component to form a final composition (Chung *et al*, 2004).

Types of flow

The two types of flow in compounding are the *shear flow* and the *elongation flow*, which is also known as the "stretching or extension flow".

Shear and elongation flow

Shear flow occurs when there is a pressure drop along a flow path. Elongation flow occurs when there is compression associated with stress. Equations 4 and 5 illustrate shear and elongation flow using the Trouton relationship (Rauwendaal, 1981).

$$F_{\text{SHEAR}} = 3\pi\eta\dot{\gamma}r_1r_2 \quad (4)$$

$$F_{\text{ELONGATION}} = 3\pi\eta\dot{\varepsilon}r_1r_2 \quad (5)$$

Where η is the viscosity, $\dot{\gamma}$ is the shear rate, $\dot{\varepsilon}$ the elongation rate, and r is the radius of a particle.

Polymer melts are highly viscous and for this reason laminar flow is common, which causes inequality in distribution. Polymer melts therefore need to be re-orientated to attain uniform distribution. Stress develops if a polymer melt is sheared or elongated. The polymer melt varies linearly with the rate of shear stress at a given time.

Distributive mixing occurs at a low shear rate. However, dispersive mixing can occur only at shear rates great enough to break up the dispersed phase.

Simple shear flow depends on the velocity gradient (γ') perpendicular to the main flow direction. This gives rise to a shear stress (τ) (Newton's viscosity law).

Above a certain Weber number value the droplets break as shear forms the droplet. The Weber number is a dimensional ratio of the shear force to surface tension forces:

$$We = \frac{\eta \gamma' d}{\sigma} \tag{6}$$

Where d is the droplet diameter, σ is the interfacial tension, γ' is the shear rate and η is the viscosity.

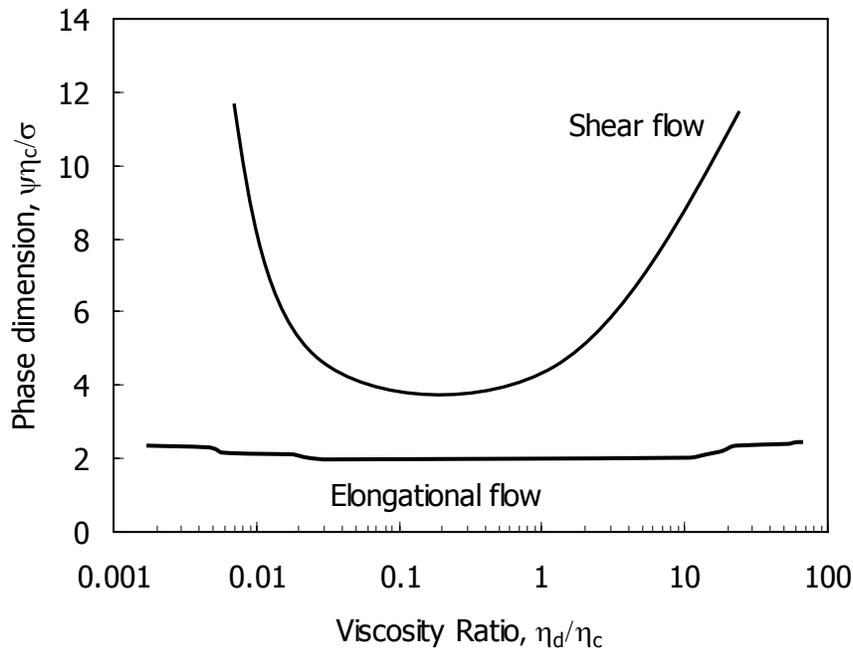


Figure 11: Schematic representation of the phase dimension of an immiscible fluid as a function of the viscosity ratio (Karam and Bellinger, 1968).

As the Weber number exceeds a critical value, droplet break-up occurs. The drop in viscosity to that of the continuous phase determines the critical Weber number. This is depicted in Figure 11, which clearly shows that the droplet diameter (d) can be reduced if the interfacial tension (σ) is lowered, the shear rate ($\dot{\gamma}$) is increased and when the viscosity of the dispersed phase (η_d) is similar to or slightly lower than the viscosity of the continuous phase (η_c). Theory predicts that above a viscosity ratio of 4, the break-up of droplets will not occur. This occurs with slightly higher viscosity ratios. For high drop viscosities, any slight deformation will cause droplet rotation, thereby preventing break-up (Karam and Bellinger, 1968).

There is a velocity gradient in the direction of the key flow in elongation flow. As there is no transverse shear component is not present, droplet rotation is not possible and very viscous drops can be deformed.

4.1 Batch mixers

Open mill

This class consists of two-roll or three-roll open mills. A two-roll mill consists of two counter-rotating rolls that can be adjusted to move closer to each other. The nip is the distance of closest approach between the two rolls. In this type of compounding, extensive elongation mixing occurs due to the extentional flow that takes place at between the rolls (Swanborough, 1979). Mixing in the axial direction must be aided by repeated “folding over” of the mass on the mill for good mixing.

Advantages of the two-roll mill

- There is good temperature control of the product since there is cooling and heating.
- There is also a greater surface area available to the polymer system.
- The region of high shear is minimal; this avoids temperature build-up.
- The degree of dispersive mixing is high.

Disadvantages of the two-roll mill

- The process is dirty and it is not easy to achieve a uniform product.
- The process takes a long time.

- It operates as an open system, which implies contact with air at high temperatures.
- Temperatures fluctuate when fillers and other materials are added (Brichall *et al.*, 1981).

Internal mixers

An internal mixing process is similar to an open mill compounding process, but it is enclosed in a mixing chamber. Three types of mixing process occur. Firstly, an intensive or dispersive mixing occurs around the tips of the rotor blade. Extensive mixing then occurs due to the shear flow and takes place between the cylindrical portion of the rotor and the chamber wall; and finally distributive mixing due to random plug convection between the two rotor tips (Hold, 1982).

The advantages of internal mixers are the versatility and simplicity of operation, and the robustness of the machines. The disadvantages include high capital cost, poor temperature control and high and uneven power load.

4.2 Continuous compounders

To meet the requirements for high throughput capacities and high quality product standards, compounding equipment has been developed, ranging from a single-screw extruder to a twin-screw extruder (Mack, 1980).

Conventional single-screw extruder

A single-screw extruder uses a combination of pressure and drag flow to pump polymer material. A conventional single-screw extruder melts and pumps material against pressure (Hold, 1982). A single-screw extruder can compound and mix because of the shear force, which moves the material through the screw channels. However, it is not a good mixer because the material that passes through the extruder is subjected to the shearing only, i.e. there is no elongational flow (Tadmor, 1970). The main advantages and disadvantages of single-screw extruders are:

Advantages of the conventional single-screw extruder

Mechanically simple, easy to operate and capable of high-pressure generation.

Disadvantages of the conventional single-screw extruder

Lack of positive transmission characteristics, inadequate compounding and homogenising capabilities.

Twin-screw extruders

The development of twin-screw extruders emerged from the limitations of single-screw extruders. There are two types, namely intermeshing and non-intermeshing extruders. Each type is further divided according to the direction in which screw rotates; it can be by co-rotational or counter-rotational. Figure 12 shows the different types of twin-screw extruder.

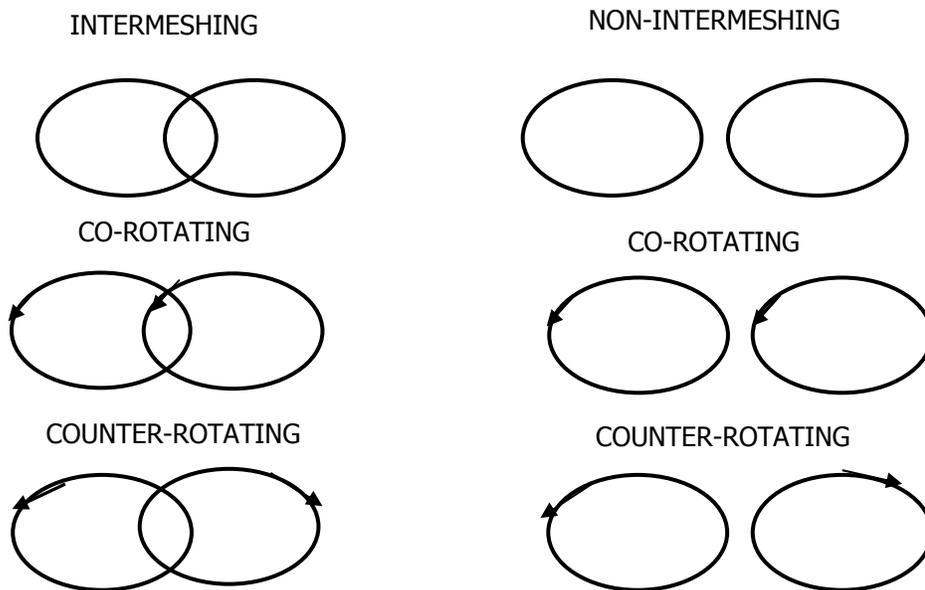


Figure 12: Typical types of twin-screw extruder (Shenoy, 1999)

Intermeshing co-rotating extruders

This type of conventional extruder is associated with positive displacement and is effectively self-wiping if kneader blocks are used (Jakopin, 1974). The co-rotation of the screws moves the material back and forth between the screws, thus allowing effective dispersive mixing (Rauwendaal, 1981). By selecting different numbers of flights, the intensity of the shearing

action can be changed. Special shearing can be arranged between screw sections to perform intensive dispersive mixing.

Advantages of twin-screw extruders

- Positive displacement gives throughput without affecting the properties of the product being processed (Rauwendaal, 1981).
- The self-wiping characteristics mean that no material is left in the machines.

Disadvantages of twin-screw extruders

- High capital cost.
- Mechanically complicated and difficult to make.

Intermeshing counter-rotating extruders

These are similar to co-rotating twin-screw extruders since both of them give positive displacement. The intermeshing point of the counter-rotating screws acts as a “calendar nip”. A small portion of material passes through the nip between the screws, while the remainder passes along the axes in closed chambers (Nichols, 1982). The residence time in an intermeshing counter-current extruder is short and therefore it is sensitive to thermal degradation of the material.

Non-intermeshing counter-rotating extruders

These are composed of two screws rotating at a given speed in different directions. The flight of one screw does not protrude into the channel of other screw; therefore this extruder is similar to a single-screw extruder, with the exception of having two screws. Because the stream of flow meets at the interface between the screws, there is more extensive mixing than in a single-screw extruder. Staging the flight of the screws can further increase extensive mixing, but this does reduce the pumping efficiency (Shenoy, 1999). Non-intermeshing counter-rotating is used only where dispersive mixing is not a necessity (Walk, 1982). Non-intermeshing counter-rotating extruders are commonly used in polymer blending, preparation of pigment concentrates, adhesives and fibreglass reinforcement.

Continuous internal mixers

Continuous internal mixers are designed to control the forward action of material through the mixer and the mixing action independently (Hold, 1982). They are composed of two sections: the mixer itself and an intensive mixing section. The mixer has a conveying section that propels the material forward and another section that moves the material in the opposite direction for intensive mixing. In the intensive mixing section, the material is dispersed through the gaps between the rotor and the chamber walls, coupled with a kneading action between the material itself and the rotor. The shear deformation and distribution that takes place within the residence time is greater in a continuous internal mixer with a non-intermeshing mixing blade than in any twin-screw extruder. The material has to be fed continuously because mixing along the axes is not effective. Since this type of compounder does not produce enough pressure to extrude the material, an extruder is always incorporated for pelletisation to take place.

Co-rotating disk extruders

Co-rotating disk extruders consist of two moving, drag-inducing surfaces. The material is conveyed by the action of the two walls and the side of the disks, which forms a wedge-shaped chamber (Tadmor, 1970).

CHAPTER 5 CHARACTERISATION TECHNIQUES

Fillers, additives, resin, paraffin and microcrystalline waxes are the ingredients used to process wax moulding compounds. This chapter describes the basic techniques used to characterise the mechanical, thermal and chemical properties of investment casting filled wax moulding compounds for quality control and to meet specific requirements for investment casting (Aibarro *et al.*, 2001).

5.1 Mechanical properties

The mechanical properties of a pattern are crucial in that a hard, brittle wax pattern may be damaged during the assembly and storage stages in the investment casting process. A wax that is too flexible and soft also may not retain its shape during shelling process. Therefore, three-point bending and impact tests are used to characterise the mechanical properties of wax to avoid the above-mentioned problems.

5.1.1 Three-point bending test

This method is used to characterise brittle materials where tensile, compression and hardness testing are problematical, e.g. very low deformation before fracture occurs. The results of the testing method are sensitive to specimen and loading geometry and strain rate. The parameters of interest are the bending stress and the maximum deflection of a beam. The modulus of elasticity and the modulus of rupture can be calculated. Figure 13 below shows the three-point bending test set-up.

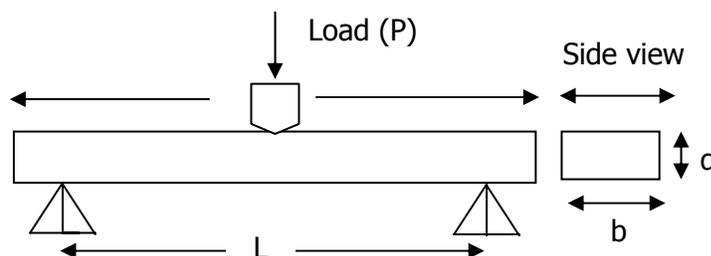


Figure 13: Three-point bending test set-up (ASTM D790, 1983)

Where P is the load, L is the support span, b is width of test beam and d is the depth of tested beam

The stress, strain, modulus of rupture and Young's modulus of bending are calculated using the following equations.

(i) Stress:
$$\sigma = \frac{3PL}{2bd^2} \quad (7)$$

(ii) Strain:
$$\varepsilon = \frac{6Dd}{L^2} \quad (8)$$

(iii) Modulus of elasticity:
$$E_B = \frac{L^3 m}{4bd^3} \quad (9)$$

Where σ_{is} stress, ε is strain, E_b is the modulus of elasticity in bending and m is the slope of the tangent to the initial straight-line portion of the load deflection curve

5.1.2 Impact testing

Impact testing is used to quantify the fracture behaviour of materials. The mechanical tests determine the ability of a material or object to withstand a high loading rate assault. Critical parameters include the fracture energy and the fracture stress. There are basically two types of impact test. Projectile methods include the drop weight test and pendulum tests include the Charpy, Izod and tensile impact test procedures (Callister, 2003).

Drop weight impact test

This method involves dropping a weight on top of a sample from varying heights. The impact energy is calculated from the mass and the drop height, i.e. potential energy. The test result depends on the nature of the damage that the specimen suffers. It can either survive, or be slightly or completely destroyed. In industrial practice, it is common to consider the results obtained from this test as either a fail or a pass at a prescribed drop height for well-defined sample and projectile geometries (ASM Handbook, 2000). In effect this is a quality control technique that is dependent on operator interpretation of the damage.

Advantages of the drop impact test

- Appropriate to moulded samples
- Failure can be expressed in terms of deformation, complete fracture or crack initiation.
- Samples do not have to shatter to be considered to have failed.

Disadvantages of the drop impact test

- Time and resource-consuming, requiring from 50 - 100 samples
- Changing the drop height causes a change in the impact velocity; this exposes a material to different strain rates.
- Causes safety and health hazards as operators need to continuously lift and drop heavy weights.
- Subject to differences in individual assessment of damage (i.e. one person a different opinion to another)

Charpy and Izod pendulum impact tests

A pendulum consists of a single arm and a striking rod, the geometry of which is dependent on the test method to be used. The drop height and mass determine the potential energy. Extra weight can be added to each pendulum unit. The Charpy and Izod impact tests are similar but differ in the ways in which the samples are prepared, notched and clamped, and in the units of measurement.

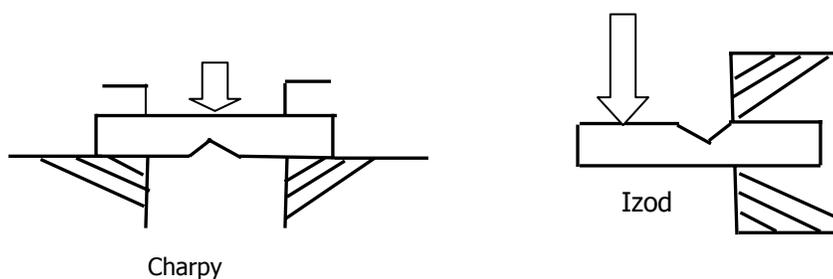


Figure 14: Charpy and impact test set up (Robert, 1985)

In notched Izod testing, the notch faces the pendulum after being mounted in a vice fixture. In Charpy testing, the sample is laid horizontally on two supports against an anvil. The sample is notched in the middle and faces away from the pendulum. This is shown in Figure 14. As the

sample breaks, the energy absorbed is calculated from the height that the pendulum has attained after breakage (Robert, 1985).

Disadvantages of the Charpy and Izod pendulum impact tests

Charpy and Izod pendulum impact tests do not provide information on what happens during impact. Furthermore, the sample can fail internally but display no damage externally (ASTM Handbook, 2000).

5.2 Dynamic mechanical analysis properties

Dynamic mechanical analysis (DMA) analyses a polymeric material's response when an oscillating force is applied to a sample. It basically determines the elastic modulus (or storage modulus, G), the viscous modulus (or loss modulus) and the damping coefficient as a function of temperature, frequency or time. From DMA, the transition regions, such as the glass transition temperature, rubbery plateau and the melting temperature, are identified. DMA is used for product and quality development in the plastics industry (Menard, 2003).

Polymers are viscoelastic materials since they exhibit both elastic behaviour just like a spring when stretched quickly returns to their original state and viscous (dashpot-like) behaviour which resist shear flow and strain linearly with time when a stress is applied. Consider the application of a sinusoidal oscillating deformation to a polymer sample the stress yields:

$$\sigma = \sigma_0 \sin(\omega t) \quad (10)$$

Where σ is the stress at given time, σ_0 is the maximum stress and ω is the frequency of oscillation.

The sample will experience a sinusoidally varying stress in the linear viscoelastic regime. Both the viscous (flow-like deformations) and elastic behaviour patterns of the material affect the resulting stress wave. Taking the derivative of equation (10) gives the rate of stress variation:

$$d\sigma/dt = \sigma_0 \omega \cos(\omega t) \quad (11)$$

Two limiting behaviours are shown by viscoelastic materials: They are represented by the perfect elastic solid and the viscous liquid. These systems are generally pictured as a Hookean spring and a dashpot respectively. The stress and strain for a Hookean spring will be in phase and the response can therefore be written as:

$$\varepsilon = E \sigma_0 \sin(\omega t) = \varepsilon_0 \sin(\omega t) \quad (12)$$

Where ε the strain at is given time, and ε_0 is the maximum stress

This curve is shown in Figure 15. It has a phase lag of value 0° and this represents the in-phase portion of the curve.

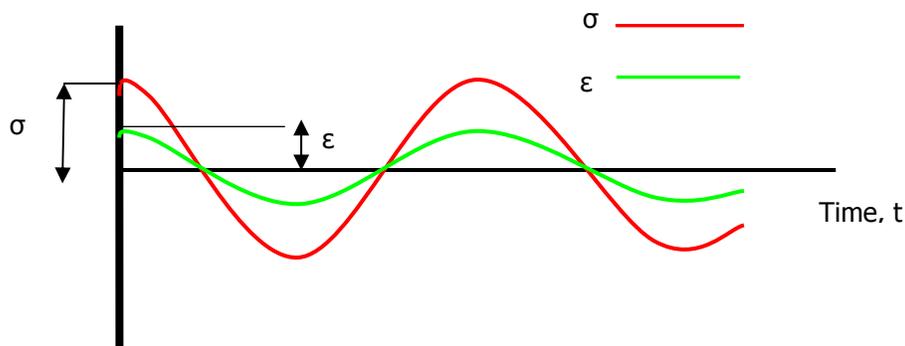


Figure 15: Perfectly elastic solid with no phase lag (Menard, 2003)

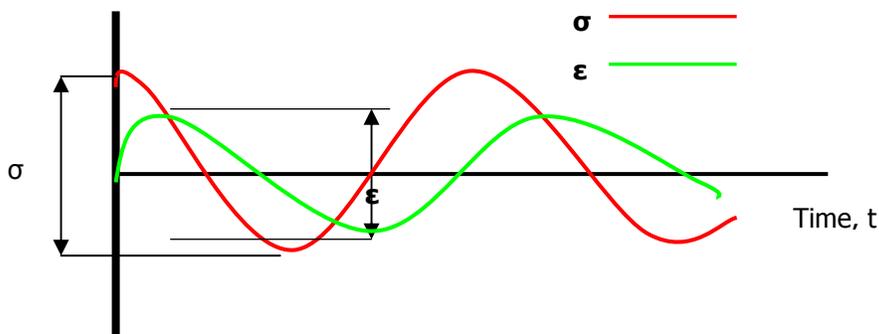


Figure 16: Purely viscous modulus at a phase angle of exactly 90° (Menard, 2003)

According to Newton's viscosity law, the stress in a pure viscous liquid is directly proportional to the strain rate, i.e. the first derivative of strain. Using a dashpot, the various responses in terms of strain rate can then be expressed as

$$\varepsilon(t) = \eta d\sigma_0/dt = \eta \sigma_0 \omega \cos(\omega t) \quad (13)$$

This can further be rewritten as

$$\varepsilon(t) = \sigma_0 \omega \varepsilon \cos(\omega t) = \varepsilon_0 \omega \sin(\omega t + \pi/2) \quad (14)$$

This curve is shown in Figure 16. The phase lag is exactly 90°.

A viscoelastic material exhibits behaviour intermediate between the viscous and elastic limits. There is a difference between the resultant strain and the applied strain at some angles. The elastic response at any time must be added by a phase angle δ ; this can be written as:

$$\varepsilon = \varepsilon_0 \sin(\omega t + \delta) \quad (15)$$

Applying trigonometry, the equation can be rewritten as

$$\varepsilon = \varepsilon_0 [\sin(\omega t) \cos(\delta) + \sin(\delta) \cos(\omega t)] \quad (16)$$

The above equation can be broken into an "in" phase and an "out" phase strain, which is depicted in Figure 17 below.

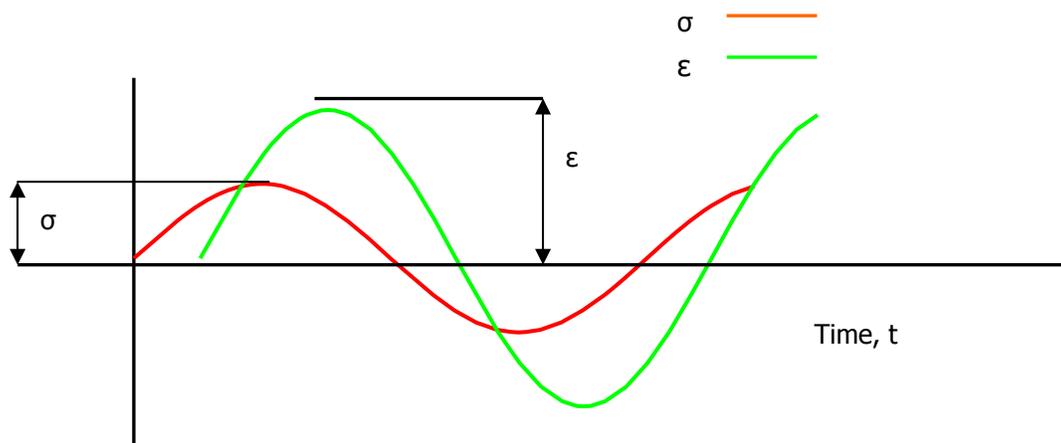


Figure 17: Viscoelastic materials (Menard, 2003)

The vector sum of these two components gives the complex strain of the sample:

$$\varepsilon^* = \varepsilon' + i \varepsilon'' \quad (17)$$

Once all the basic properties are known, all the other properties can be calculated from them.

Table 8 shows the calculation of the remaining properties by DMA.

Table 8: Calculation of material properties by DMA (Menard, 2003)

Property	Formula
Strain	$\varepsilon = \varepsilon_0 e^{i\omega t}$
Stress	$\sigma = \sigma_0 e^{i(\omega t + \delta)}$
Damping	$\tan \delta = \frac{E''}{E'} = \frac{\sin(\delta)}{\cos(\delta)}$
Complex modulus	$E^* = E' + iE''$ $ E^* = \sqrt{E'^2 + E''^2}$
Complex shear modulus	$G^* = \frac{E^*}{2(1+\nu)}$
Complex viscosity	$\eta^* = \frac{3G^*}{\omega} = \eta'' + i\eta'$
Complex compliance	$J^* = \frac{1}{G^*}$
Work stored	$\frac{\varepsilon_0 \sigma_0 \cos \delta}{2}$

Where σ_0 is the maximum stress, ω is the frequency of oscillation, ε_0 is the maximum stress, E' is the storage modulus, E'' is the loss modulus and δ is the phase angle.

5.3 Thermomechanical analysis properties

5.3.1 Thermodilatometry

Most, if not all materials, including investment casting waxes, expand with increasing temperature. Larger volumetric changes are observed during phase changes. Such effects can be problematic with respect to pattern materials as it could cause the mould shell to crack.

Thermal expansion and volume changes are measured using dilatometers. In a typical set-up, a sample is heated at a constant-temperature scan rate in an oven and the dimensional changes are monitored via the displacement of a probe in contact with the sample. The coefficient of linear thermal expansion is defined by:

$$\alpha = \frac{1}{L} \frac{dL}{dT} \quad (18)$$

Where L is a measured length dimension and T is the temperature.

5.3.2 Volumetric expansion

This methodology determines over a range of temperatures the volumetric expansion characteristics of wax patterns. Commercial instruments are available that can generate profiles of volume versus temperature (Monk, 2001).

5.4 Physical properties of waxes

Waxes are classified as “soft” or “hard” depending on whether they can be worked by hand or whether a tool is required. “Hard” waxes are preferred for patterns because soft waxes will deform more easily.

5.4.1 Melting/softening point

Many waxes are highly crystalline and their melting points can be used to distinguish them. In industry there is an additional connotation associated with “melting”, i.e. the temperature at

which the wax becomes sufficiently fluid to be processed. These “melting points” of wax patterns can be determined by using either the ring-and-ball softening point or the Ubelhode drop melt point.

Ring-and-ball softening point. In this method the wax is placed in a water bath and a ball-bearing is placed on top of it. The temperature of the wax is increased until the wax softens enough to let the bearing penetrate through it.

Drop melt point. In this method the wax is placed in a special cup with a small opening and the temperature of the wax is raised until the first drop falls. The softening point indicates the temperature at which the wax changes from solid to liquid. It basically describes the temperature at which the wax is dewaxed during the investment casting process (Monk, 2001).

Congealing point. This is the temperature at which the waxes will not flow under gravity. Softer waxes will flow easily, while harder waxes tend not to bend or deform – hence there are more dimensionally consistent. To avoid pattern deformation, it is advisable that wax should be injected at a temperature 4 - 5°C below the congealing point.

5.4.2 Dimensional analysis

This is used to determine the dimensional stability of wax patterns after injection moulding. Wax is injected into a tool of given dimensions; the wax is cooled at a given controlled temperature. A calliper is then used to measure the length and thickness and this is compared with the tool dimensions and tolerance specification (Monk, 2001).

5.4.3 Density

Density measurement is important in investment casting moulding compounds in that a high density allows fillers to be separated easily from the base wax, to allow the base wax to be reclaimed and reused. It also gives an indication of the degree of mixing achieved.

Actual density can be measured using the Archimedean Principle (Spieweck and Bettin, 1992). This principle states that a solid body immersed in a liquid loses as much of its own weight as the volume of the liquid it has displaced.

$$\rho_s = \frac{A}{A - B} \rho_L \quad (19)$$

Where A is the weight of the sample in air, B is the weight of the sample immersed in water, ρ_s is the density of the sample and ρ_L is density of liquid. The theoretical densities (ρ_c) of the blend were determined using the mixing rule for non-interacting components:

$$\rho_c = \left(\sum_{i=1}^n \frac{w_i}{\rho_i} \right)^{-1} \quad (20)$$

Where ρ_i is density of the component and w_i is the weight fraction of component.

5.5 Thermal properties

5.5.1 Differential scanning calorimeter (DSC)

A DSC design consists of a heat flow path, two pans of which one contains the polymer and one is left empty to act as a reference. These two components are connected to a computer. Using the DSC, the heat capacity can be determined by plotting the difference in heat flow against temperature. The heat flow is heat supplied per unit of time, and the heating rate is the temperature change per unit of time

The heat flow divided by the heating rate gives the heat capacity:

$$C_p = \left(\frac{dq}{dt} \right) / \left(\frac{dT}{dt} \right) \quad (21)$$

Where q is the heat supplied, t is the time and T is the temperature.

DSC can detect the glass transition of a crystalline polymer. When heat is absorbed, the polymer undergoes a glass transition – indicated by a change in its heat capacity. This is depicted in Figure 18.

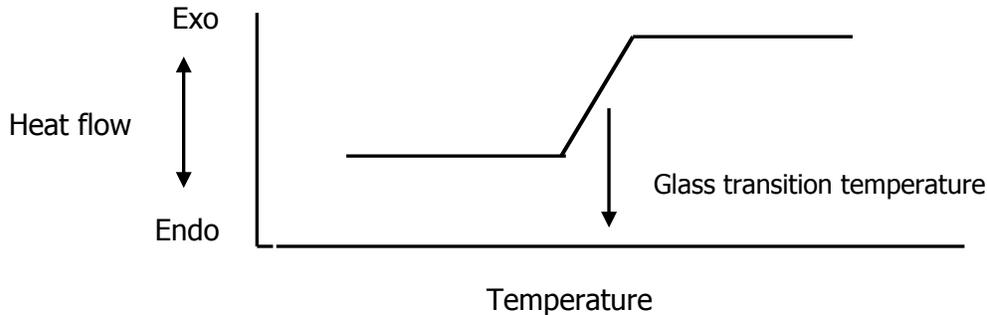


Figure 18: Heat flow against temperature showing glass transition

Above the T_g , the mobility of the polymer chain increases. Above a certain temperature, the chain gains enough energy to form very orderly, refined arrangements called crystals. The formation of crystals gives off heat. Figure 19 shows a plot of heat flow against temperature, with a pronounced peak.

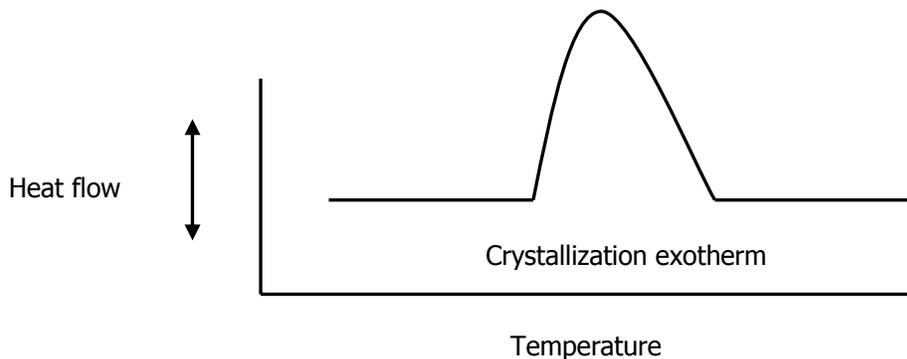


Figure 19: Heat flow against temperature showing crystallisation temperature

The temperature at the highest peak is the crystallisation temperature (T_C). The latent energy of crystallisation can be calculated from the area under the peak. As more heat is added above T_C , the polymer melts and its crystals begin to fall apart. The chains are in disordered arrangement and move around freely. This is shown in Figure 20 below.

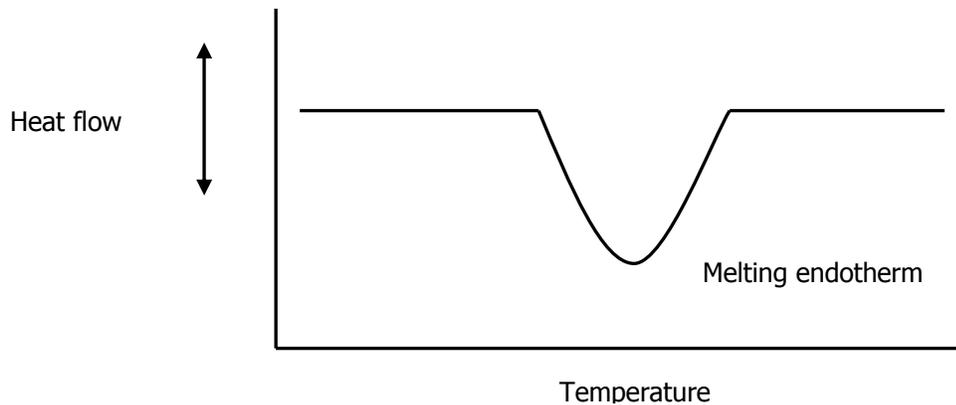


Figure 20: Heat flow against temperature showing melting temperature

DSC can be used to calculate the % crystallinity of a polymer using the heat of melting. The heat of melting can be determined from the area under the melting peak.

$$Area = \frac{heat \times Temperature}{time \times mass} = \frac{JK}{sg} \quad (22)$$

Where the units are such as joules x Kelvins x (seconds)⁻¹ x (grams)⁻¹:

If the area is divided by the heating rate it is then possible to predict the heat given off when a polymer melts.

$$\frac{Area}{Heating \ rate} = \frac{\frac{JK}{sg}}{\frac{K}{s}} = \frac{J}{g} = H_m \quad (23)$$

The energy in joules can be determined by multiplying it by the mass of the known polymer. The heat given off by the part of the polymer sample that was already in the crystalline state before it was heated above T_c equals the total heat given off during melting, minus the heat of crystallisation (Dean, 1995):

$$H' = H_m - H_c \quad (24)$$

5.5.2 Thermogravimetric analysis

The ash content of a wax pattern may be important. This is because an ash content of more than 3% can cause mould reaction during investing process and poor surface finish. Thermogravimetric analysis (TGA) is used to measure the change in mass of a sample against temperature and time. TGA further provides information about the thermal stability of a chemical and its composition. In wax patterns, this measurement includes oxidative stability, decomposition kinetics, moisture and volatile contents, and shelf-life studies using kinetics.

5.6 Rheometry and melt flow index

Viscosity (η) is a measure of the resistance to any deformation. When a shear stress is applied to a solid body, the body deforms until the deformation results in an opposing force to balance that applied, resulting in equilibrium. Even among fluids (i.e. substances that are accepted as fluids), there can be wide differences in behaviour under stress. The value of the viscosity is constant for fluids obeying Newton's law. Such fluids are known as Newtonian fluids. If η is constant, the shear stress is linearly dependent on the velocity slope. This is accurate for most common fluids.

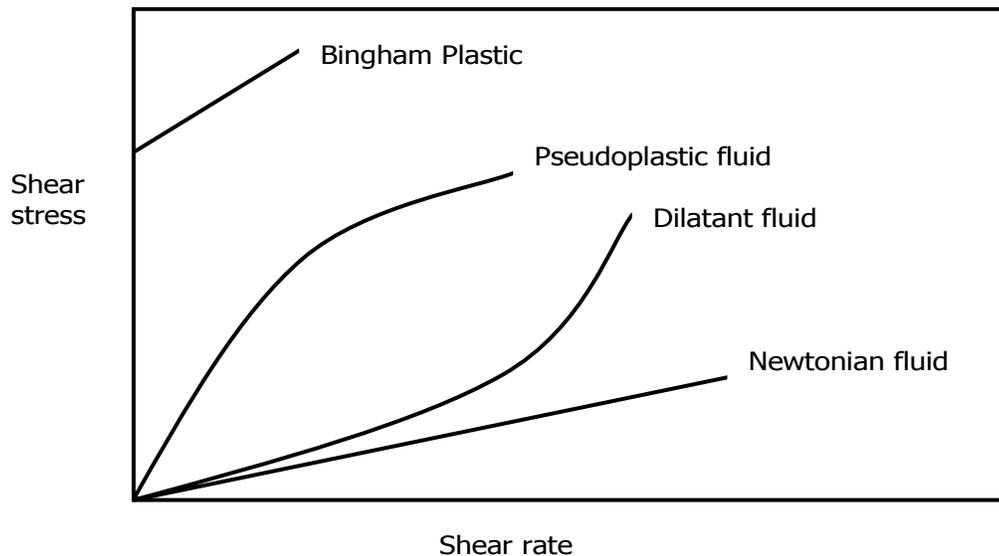


Figure 21: Shear stress vs. rate of shear strain of fluids

For non-Newtonian fluids the value of the viscosity is not constant. There are several examples of these, and they are outlined briefly below.

These categories are based on the relationship between shear stress and the velocity slope (rate of shear strain) in the fluid. These relationships can be seen in Figure 21 above for several categories.

Each of these lines can be represented by the equation:

$$\tau = A + B\dot{\gamma}^n \quad (25)$$

where A , B and n are constants. For Newtonian fluids $A = 0$, $B = \eta$, $n = 1$ and $\dot{\gamma}$ is the shear rate.

Below are brief descriptions of the physical properties of the several categories:

- *Plastic*: Shear stress must reach a certain minimum before flow starts.
- *Bingham plastic*: These fluids do not flow unless the stress applied exceeds the "yield stress". Typical examples include sewage sludge, tomato paste and toothpaste.
- *Pseudo-plastic*: These fluids exhibit a decrease in viscosity with increasing shear rate and hence are often referred to as "shear-thinning fluids". Typical examples include polymer melts, polymer solutions, blood and filled polymer melts.
- *Dilatant substances*: These fluids show an increase in viscosity with increasing shear rate and are "shear-thickening fluids". Typical examples consist of wet sand, starch suspension and gum solution.

Rheology is the study of the deformation and flow of matter (Lenk, 1978). It describes the interrelation between force, deformation and time. The term comes from the Greek word *rheos*, meaning "to flow". From a broad perspective, rheology includes almost every aspect and behaviour that deals with the deformation of materials as a result of an applied stress. In other words, it is the study of the internal response of materials to external forces. Rheology can be applied to all materials, from gases to solids, regardless of their type physical state, or the form in which they are used.

Fundamental to rheology are the concepts of material elasticity and viscosity. Materials will respond to an applied force by exhibiting either elastic or viscous behaviour or a combination of both mechanisms. Solids store mechanical energy and are elastic, whereas fluids dissipate energy and are viscous. The combined behaviour is termed *viscoelasticity*. Common to liquids, solids and substances which are viscoelastic is the phenomenon that if a stress is applied to them, they will strain. If solids are elastic, they deform and return to their original shape. Since fluids are not elastic and, hence, are viscous, their deformation is irreversible.

Rheology is used to describe the properties of a wide variety of materials such as investment-casting waxes. Rheometers are used in the industry at various levels of sophistication to provide information for different purposes, such as quality control, product development and process engineering. The measurements obtained are used to obtain correlations between molecular structure and material properties, and between material properties and behaviour in practical situations. This requires sophisticated mathematical treatments using data obtained from simple rheological experiments. Without rheology, nothing in materials and process engineering can function today.

In a rotational viscometer, a polymer melt is sheared between rotating cylinders, cones or plates, under controlled-stress or controlled-rate conditions (Shenoy & Saini, 1984). There are two types of mechanism for measuring viscosity in rotational rheometers, namely controlled-stress and controlled-rate rheometers. In a controlled-stress rheometer, the torque/shear stress is set and the strain rate is determined. In a controlled-rate rheometer, the shear rate is set and the resulting shear stress is measured. The rheometer geometry and the device used to apply a constant torque or rotation speed determines the type of rotational rheometer (Gebhard, 2000). Rheometers are of three basic geometry types, namely the concentric cylinder, the cone and plate, and the parallel plate. These are shown in Figure 22.

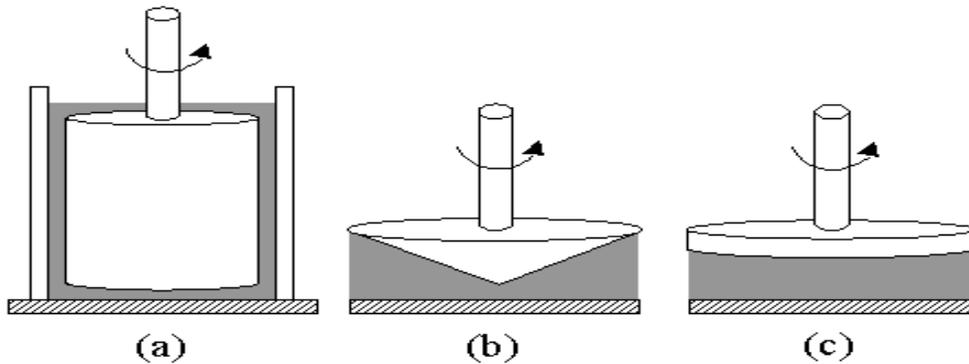


Figure 22: The three types of rheometer geometries: (a) concentric cylinder, (b) cone and plate and (c) parallel plate

For a cone-and-plate rheometer, the shear rate and the shear stresses can be calculated mathematically. The polymer melt is sheared between the cone and the flat plate at a very small angle. Consider a polymer melt or fluid that lies between the plate and the cone with an angle of β , which is normally between 2° and 8° and with a radius R , as shown in Figure 23. Clearly, the speed of the plate and the angle β determine the shear rate (Fenner, 1980).

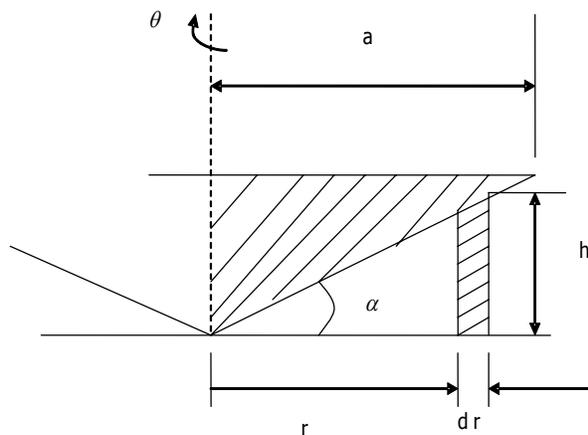


Figure 23: Cross-section of a cone-and-plate rheometer

As the angle is small, the expected flow is shear flow and at steady state condition, the relative velocity between the surfaces is $R \Omega$, where

$$\Omega = \frac{d\theta}{dt} \quad (26)$$

In this expression, θ is the angular displacement of the cone and t is the time.

Hence, the shear rate is given by

$$\dot{\gamma} = \frac{R\Omega}{H} = \frac{R\Omega}{R \tan(\alpha)} = \frac{\Omega}{\tan(\alpha)} \approx \frac{\Omega}{\alpha} \quad (27)$$

Since $\tan(\alpha) = \alpha$ is valid for a small angle, α must be small enough to ensure a shear flow. The shear stress applied is a product of the torque area in the element, $2\pi r dr$, and the distance from the axis of rotation, R . Hence, the total torque applied to the cone is given by:

$$\tau \int_0^a 2\pi r^2 dr = \frac{2}{3} \pi a^3 \tau \quad (28)$$

The torque is equal to the product of the load, W , and the radius of the appliance, b . Therefore, shear stress can be expressed as follows:

$$\tau = \frac{3Wb}{2\pi a^3} \quad (29)$$

The cone-and-plate rheometer has the advantage of being able to measure shear rate and shear stress simultaneously, and therefore can measure both Newtonian and non-Newtonian fluids. Rotational methods can also incorporate oscillatory and normal stress tests for characterising the viscoelastic properties of samples (Kosinski & Caruthers, 1986).

The simple shear flow assumption becomes invalid at high rotational speeds due to secondary flows and instabilities, such as the tendency for cavities to form in the melt near the edge of the cone. Therefore, the reliability of rotational rheometers is restricted.

Rotational rheometers typically operate in the shear rate range 10^{-2} to 5 s^{-1} . In polymer processing practice, much higher shear rates may be found. The applicability of rotational rheometers is therefore limited to characterising materials in the low shear rate range (Fenner, 1985).

Melt flow index

Melt flow indexers are simple capillary viscometers that are used mainly as a quality control technique to characterise the viscosity of polymer melts (Ives, 1971). The conventional technique (ASTM Standard D1238) is as follows: Solid polymer is fed into the hot barrel shown as in Figure 24. When the desired temperature is reached, a fixed weight is placed on top of the piston and the melt is forced out of the die. The mass flow rate of the extrudate is measured and reported in grams per ten minutes.

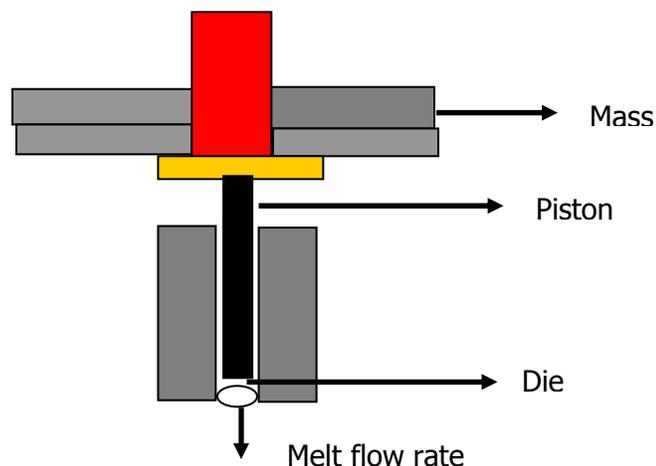


Figure 24: Melt flow indexer

ASTM Standard D1238 prescribes a die diameter of 2,095 mm and a weight of 2,16 kg for polyethylene and polyethylene copolymers such as EVA.

Advantages of the melt flow indexer

- Flow rate measurement is inexpensive and the flow can be measured without difficulty.
- The melt flow index is a standard ASTM measurement.

Disadvantages of the melt flow indexer

- The melt flow index results are not true reflections of viscosity as the capillaries are short and the entrance and exit effects are therefore not negligible.
- Materials may start to degrade chemically before the actual start of the test when they are heated in the barrel for 5 to 10 minutes.
- Inaccurate results are obtained when air is entrapped or if the polymer melt is not fully molten.
- Filler can drop out of the suspension and inaccurate result might be obtained.

5.7 Implications for the development of a urea moulding compound

The prime objective of this study was to develop an alternative to the conventional cooking process for the manufacture of urea moulding compounds. Based on the literature search, it was decided to explore a polymer compounding technique. The main requirement for the new process is increased productivity by reducing the manufacturing time to a minimum while keeping the material cost down by choosing appropriate raw materials and formulations. The material properties were further characterised to check that they do meet the specific requirements of investment casting.

Several screening experiments were done with respect to the raw materials, i.e. the polymer, the wax and the process equipment.

The polymers used were:

- Polyethylene glycol (PEG)
- Polyvinyl alcohol (PVOH)
- Ethylene vinyl acetate (EVA).

PEG was used because it is compatible with PVOH and forms inclusion compounds with urea. Through careful literature research it was concluded that PEG 6000 forms a compatible blend with PVOH only if dissolved in a solution of DMF at a temperature above 70°C. This means that this process in effect returns to the original cooking process, so it was later abandoned.

The concept of eutectics was employed as a possible area of exploration for forming eutectic complex investment casting moulding compounds. Forming a urea-eutectic complex investment-casting compound would reduce the mould temperature and reduce cost.

The following compounds are capable of forming eutectics with urea: benzoic acid and acetamide. The eutectic composition was established by creating different compositions of urea with either benzoic acid or acetamide using a thermocouple apparatus, which determines the melting and crystallisation temperatures.

Process screening experiments were performed to determine the best conventional method to be used to synthesize urea-based investment-casting moulding compounds. A conventional single-screw extruder was used to process a sample containing a mixture of urea, benzoic acid and PEG. However, it was found that it was impossible to compound the mixture since urea degrades just above its melting point to produce CO_2 and NH_3 gas. The experiment was also too dangerous as it could cause an explosion, and it was immediately stopped for safety reasons.

It was then concluded that to synthesise urea-based compounds, the material has to be processed just below its melting point. Thermoplastics such EVA, nylon and PVOH, which have low melting points, were the main possible polymers for use in making urea-based moulding compounds. The main lubricants considered for the work were:

- Stearic acid,
- Paraffin wax,
- Synthetic wax
- Stearic acid soaps

For reasons of cost-effectiveness, EVA was chosen as the possible polymer to be used. Paraffin wax, which is cheap, being manufactured by Sasol South Africa, is also very compatible with EVA and was chosen as the lubricant to be assessed.

A blend of urea prill, paraffin wax and EVA was compounded using a single-screw extruder. From the first trial, the extrudate produced blend-containing prills of urea with EVA. It was also established that a single-screw extruder does not perform dispersive mixing to reduce the prill

to a small size for good mixing. Milled urea was used to ensure more efficient dispersive mixing in the single-screw extruder. However, no success was achieved in compounding the urea-wax-EVA blend. It was then decided to use a co-rotating twin-screw extruder. There was much concern about not damaging the screws of the twin-screw extruder as these are expensive items of equipment and too costly to repair; a twin-screw extruder was therefore rented. It was definitely preferable to use milled urea. The use of a two-roll mill was also considered, since two-roll mills are more economical to use and they offer better dispersive mixing due to elongation flow.

In all the compounding trials, it was possible to compound the urea-EVA-wax blend using either a co-rotating twin-screw extruder or a two-roll mill without any difficulty. However, some of the compounds formed in the trials could not be injection-moulded.

PVOH is an attractive “biodegradable” polymer used in different areas of science and technology, especially in adhesives for paper, wood, textiles, food and pharmaceuticals. However, a polyvinyl alcohol melts and decomposes just above its melting point. Plasticisation technology was applied to lower the melting point of PVOH to allow and improve its processability. Lowering the melting point of PVOH also allows milled urea and other polymer additives with poor thermal stability (low melting points) to be processed with PVOH.

In all the compounding trials, it was possible to compound the urea-PVOH-wax blend using a two-roll mill without any difficulty. However, some compounding trials were not tried using a twin-screw extruder. It was also possible to injection-mould all the urea-PVOH-wax blends without any difficulties.

Based on the many screening experiments done, EVA was chosen as the base polymer to be compared with the PVOH used in the current system. An advantage of EVA is that the plasticisation process is avoided, unlike when using PVOH. A disadvantage of EVA is that, unlike PVOH, it is non-biodegradable and this may therefore have implications for waste disposal. PVOH is also cheaper as it is used in very small amounts compared with EVA.

CHAPTER 6 MATERIALS AND SAMPLE PREPARATION

6.1 Materials

Two different urea-polymer systems were investigated as potential compoundable moulding compounds:

- Ethylene vinyl acetate (EVA)
- Glycerine plasticised PVOH.

In each case paraffin wax was used as lubricant. The raw materials used are described in Table 9.

Table 9: Virgin polymers and their suppliers

Item	Grade	Density kg/m ³	Description	Supplier
Urea	Fertiliser grade	1 340	Melting point: 133°C Decomposition temperature: 133°C pH: 7.1 - 8.4	Algro Brits
PVOH	Celvol 504	640	Melting temperature: 133°C Degree of hydrolysis (%): 87 - 89 Viscosity 4% solution@ 23°C: 55-70 cps pH: 4.5 - 6.5	Celanese
EVA	Elvax 210	951	Vinyl acetate content (wt %): 28 MFI: 400 dg/min @ 190 °C/2,16 kg Tensile strength: 2.8 MPa Elongation at break (%): 800 - 1,000	DuPont
Wax	M3X		Melting point: 60 - 65°C Penetration (0.1 mm): 17 - 24 Oil content (%): 2.4 - 3.4	Sasol Schumann
Glycerol	CP grade	1 260	Boiling point: 290°C Melting point: 18°C	Promark Chemicals

The formulated compositions were compounded using a conventional extrusion process and a two-roll mill. Both the patterns were injection moulded.

Both the patterns were characterised using the same approach to meet the requirements for investment casting. The characterisation techniques are fully explained in Chapter 7. The experimental design and sample preparation methods used to produce the PVOH, EVA and cooked urea-based moulding compounds are fully explained in this chapter.

Finally, the results obtained from characterisation techniques were compared with the industrial cooked urea-based pattern to see if the moulding compound would meet the specified requirements. The method of preparing and compositions of cooked urea based moulding compounds is shown in Appendix D.

6.2 PVOH urea-based moulding compounds

6.2.1 Experimental design

A ternary system using urea, plasticised PVOH and wax was designed to formulate the composition necessary for exploration. The formulations explored in the ternary system are depicted in Figure 25. All compositions are on a mass basis unless otherwise indicated. The exception is the plasticiser content of the PVOH, where the technical usage of phr (parts per hundred of resin) was adopted. The formulations explored are further described in Table 10.

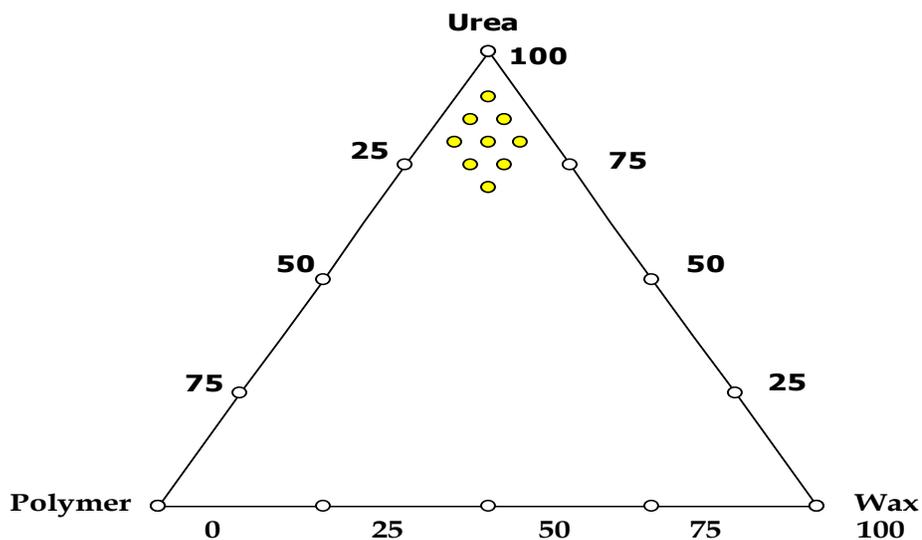


Figure 25: The ternary phase diagram showing compositions explored

Table 10: The compositions explored to make the PVOH urea-based compounds

Experiment	Urea (mass %)	Polymer (UP4) (mass %)	Wax (mass %)
A	90	5	5
B	85	10	5
C	80	15	5
D	85	5	10
E	80	10	10
F	75	15	10
G	80	5	15
H	75	10	15
I	70	15	15

Note: The experiments were repeated using UP8 (PVOH urea-based moulding compound of plasticisation degree 80)

6.2.2 Sample preparation

Figure 26 outlines the experimental procedure followed for the preparation of the biodegradable PVOH urea-based moulding compound. Urea prills were milled down to a particle size of ca. 150 μm using a laboratory milling machine (Polymer Chip Grinder, Engineering Works). PVA was impregnated with glycerine as follows:

- The PVOH powder was hand-mixed with the glycerol using a stirring rod.
- The mixture was then conditioned in a laboratory oven at 80°C for 8 h.
- These PVOH/glycerol blends were then compounded in a laboratory two-roll mill set at a temperature of 110°C.
- Once the PVOH mixture had fluxed, the mixture of urea and wax powders was added portion-wise and mixed in.

The operating conditions are detailed in Table C2 in Appendix C. Mixing was terminated once a homogeneous blend had been obtained, as judged by the human eye.

The adjustable nip between the two counter-rotating speed rolls was then set at a 5 mm gap and the product rolled into a sheet form. The sheets were pelletised using a granulator. These were then injection-moulded on an Engel 3040 machine with an 800 kN force. Typical barrel temperatures, from the feeding zone to the nozzle, were varied between 100 -110°C. The injection-moulding parameters had to be optimised for each sample as the fluidity and processability varied significantly between the different formulations. Typical process conditions are given in Table C3 in Appendix C.

At least 12 test specimens were moulded for each formulation. The moulded tensile specimens had dimensions of 4.0 x 10.0 x 80 mm. These samples were used for three-point bending testing, Charpy impact testing and dynamic mechanical analysis.

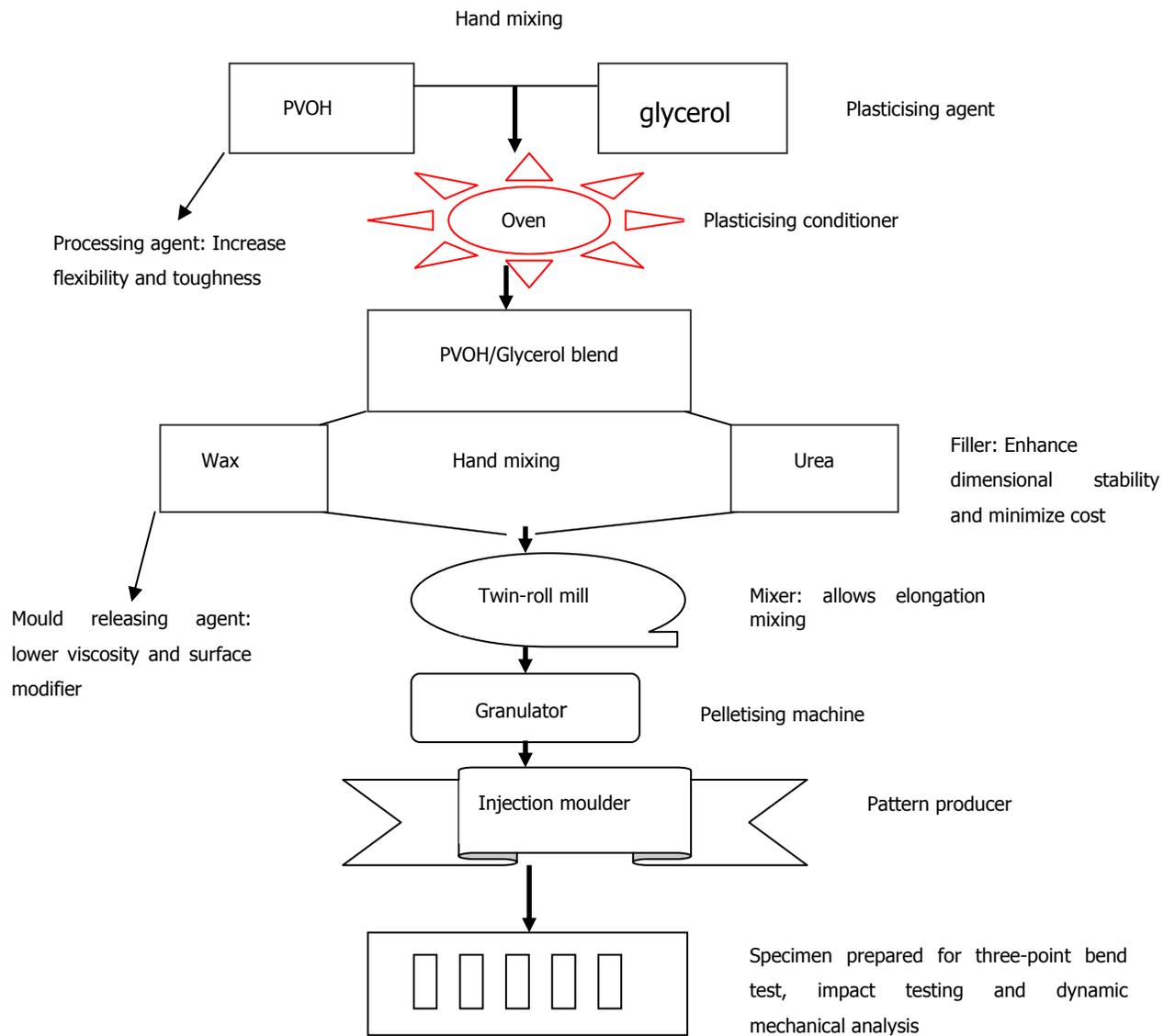


Figure 26: Outline of the preparation procedure used to produce the PVOH Urea-based compounds

6.3 EVA urea-based moulding compounds

6.3.1 Experimental design

A ternary system was designed to formulate the compositions necessary for exploration. The formulations explored are tabulated in Table 11.

Table 11: Compositions explored for the synthesis of EVA urea-based compounds

Experiment	Urea (mass %)	EVA (mass %)	Wax (mass %)
A	80	15	5
B	80	10	10
C	80	5	15
D	75	20	5
E	75	15	10
F	75	10	15
G	70	25	5
H	70	20	10
I	70	10	15
J	65	20	15

6.3.2 Sample preparation

For the development of a urea-based pattern, urea prills were milled to a size of 150 μ m using a laboratory milling machine.

The compounding of urea/EVA/wax/blends was done on a Berstorff co-rotating twin-screw extruder. The operating conditions are specified in Table C1 in Appendix C. The strands were pelletized to produce pellets for injection moulding using a granulator. Six pieces of each composition were made under the processing conditions given in Table C3 in Appendix C. Moulds for tensile strength testing were made with the following dimensions: 4 mm x 10 mm x 80 mm. The samples were to be used for the three-point bending test, Charpy impact testing and dynamic mechanical analysis to characterise the mechanical and viscoelastic properties of the pattern. An outline of the preparation of the EVA urea-based compound is shown in Figure 27.

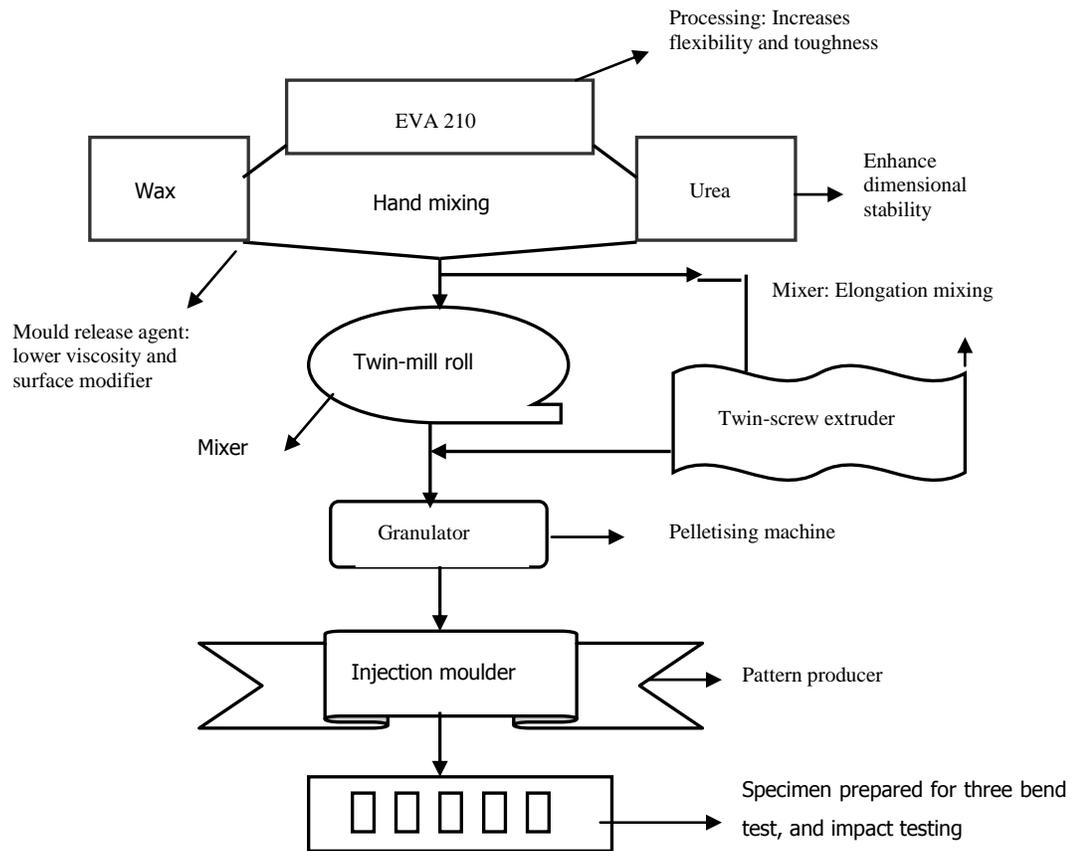


Figure 27: Outline of the preparation procedure used to produce the EVA urea based compounds

6.3.3 Determination of the urea-acetamide phase diagram

The phase diagram of the urea-acetamide system was determined using the cooling method as described by Walbrugh (2006). The results of these experiments are presented in Figure 3, Chapter 3. This work was done because it was initially believed that it would be necessary to use a urea eutectic to lower the possible processing temperature in order to avoid degradation of the urea during the compounding and shaping processes. It turned out that this was not necessary.

CHAPTER 7 CHARACTERISATION OF THE COMPOUNDS

Filled investment casting patterns form complex blends, which contain the following ingredients: fillers, resins and paraffin wax. These ingredients are used to develop the desired pattern to meet the specific requirements of an investment caster. Both compounds were analysed and the results were compared with the industrial cooked urea-based pattern using the characterisation techniques described below.

7.1 Mechanical properties

7.1.1 Three-point bending test

The three-point bending test was performed to determine the mechanical properties of the urea-based compounds. Six samples of dimensions 4 mm x 10 mm x 80 mm of each type of formulation prepared were tested in accordance with ASTM Standard D790. The samples were stored under ambient conditions for 24 h. Lloyd Instruments Instron Series IX for automated material testing, of capacity 5 kN, was used to apply the load over a 64 mm span, linked to a PC. All tests were performed using a cross-head speed of 1.8 mm/min. The value of "maximum load, maximum deflection" was used to calculate the Young's modulus of bending and the modulus of rupture. The results of the tests were processed using the equations given in Chapter 5.

7.1.2 Impact strength

Charpy impact tests were employed to obtain a qualitative indication of the material toughness. Charpy impact resistance was determined using a pendulum machine (Zwick) with a weighing capacity varying from 10 - 40 kp.cm. Ten unnotched specimens of dimensions 50 mm x 10 mm x 4 mm (length x width x thickness) were cut and machined from injection moulded tensile testing specimen.

7.2 Dynamic mechanical analysis

The injection-moulded patterns were cut and machined into rectangular bars of dimensions 10 mm x 10 mm x 4 mm (length x width x thickness). Dynamic mechanical analysis (DMA) was done on an instrument (Perkin-Elmer DMA 7e) at temperatures ranging from -50 to 150°C at 10 Hz.

7.3 Thermomechanical analysis

The injection-moulded patterns were cut and machined into rectangular bars similar to those prepared for DMA. Thermomechanical analysis (TMA) was done using the Vicat softening point which defines the softening temperature as the point at which the probe penetrates by 1 mm. TMA analysis was done at temperatures ranging from 25 to 150°C, at a heating rate of 5°C per minute using a static force of 1N and a probe with a diameter of 1 mm.

7.4 Thermal properties

7.4.1 Differential thermal analysis and thermogravimetric analysis

A small amount of sample (10 - 15 mg) was used. The tests were conducted in liquid nitrogen and the samples were heated from 25 to 800°C at a heating of 10°C per minute.

7.4.2 Differential scanning calorimetry

Thermal analysis was performed from 30 to 140°C at a heating rate of 5°C/min under liquid nitrogen using a differential scanning calorimeter (DSC) (Perkin-Elmer 7). The temperature was maintained for 1 minute and was then decreased to room temperature at a cooling rate of 5°C per minute.

7.5 Melt flow index

Melt flow index (MFI) measurements of the urea-based patterns were obtained in accordance with ASTM Standard D1238 (Procedure A) at 110°C using a 2,16 kg load. The MFI apparatus was purged before the next sample was tested to ensure accuracy.

7.6 Scanning electron microscopy

The surface morphology of the investment casting patterns was studied using a JEOL scanning electron microscope (SEM) at 10 kV. The surfaces of the patterns were coated with gold for photographic purposes.

7.7 Density

Actual density was measured using the Archimedean Principle. (This principle states that a solid body immersed in a liquid loses as much of its own weight as the weight of the liquid it has displaced.) The sample was first weighed dry in air and then weighed while immersed in water and ethanol in the case of both the EVA urea-based compound and the PVOH urea-based compound. This was done using a pycnometer. The way the measurement and calculation was done is fully shown in Appendix H.

CHAPTER 8 RESULTS AND DISCUSSION

The results obtained from the various experiments carried out are discussed in this chapter. To begin with, the process results are discussed. The main aim was to establish the effect of the composition (polymer and wax content) on the mechanical, thermal, flow, expansion and surface texture properties of the urea moulding compounds. Two-way ANOVA was used as a statistical tool to analyse the experimental results. The Charpy impact test results are used to explain how the two-way ANOVA procedure was applied in this study. The results obtained on the properties are then compared against the industrial benchmark, i.e. the “cooked” urea-based moulding compound. This is shown in Appendix E.

8.1 Process results

8.1.1 Oven

After heat treatment for 8 hr in an oven at 80°C, the PVOH powdered granules had absorbed all of the glycerol plasticiser. The glycerol had diffused into the PVOH. The processing temperature was sufficiently low to allow direct compounding with urea.

8.1.2 Single-screw extruder

Trials were initially done using a single-screw extruder. It was difficult to extrude EVA compounds but it proved impossible to compound the PVOH system. This is attributed to the high melt viscosity of the latter. A single-screw extruder is not a suitable mixer for the urea/PVOH/wax blend because it mixes by means of a shear mechanism without an elongational flow component. Shear mixing is inefficient when there is a large difference in the melt viscosities of the components.

8.1.3 Two-roll mill

It was possible to compound the urea/PVOH/wax blend using a two-roll mill. This is because this type of compounding allows extensive mixing to take place due to the elongational flow that occurs at the entrance of the nip.

8.1.4 Intermeshing co-rotating twin-screw extruder

EVA urea-based moulding compounds were successfully compounded using a co-rotating twin-screw extruder. The twin-screw compounder was a suitable mixer as the kneader blocks provide for elongational mixing. However, it proved difficult to pull the weak EVA strands directly into the pelletising unit.

8.1.5 Injection-moulding

The pelletised urea/PVOH/wax blend was injection-moulded into tensile test specimens without mould-release problems. However, at a high glycerol content the parts started to stick to the mould's surface.

In the case of EVA-based moulding compounds, it was difficult to injection-mould blends containing 80% or more of urea. This could be because the urea content has reached its critical filler level, where there is not enough EVA and liquid wax to fill the voids between the urea particles. However, injection-moulding was easily achieved at a urea content of 70% with all EVA and wax combinations.

8.2 Thermal properties

8.2.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) can be used to measure a number of characteristic parameters of a sample. Using this technique it is possible to observe the glass transition

temperature (T_g) and the melting temperature, and also fusion and crystallisation events. In this section DSC was applied to study the thermal behaviour of urea-based moulding compounds during heating and cooling. This can aid the understanding of the processing conditions needed to process the urea moulding compounds.

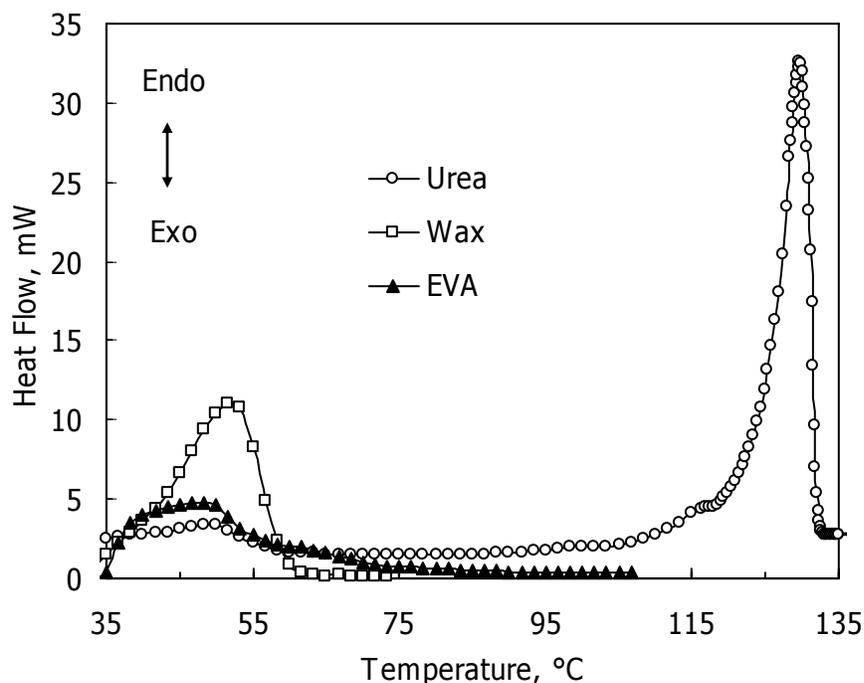


Figure 28: DSC heating curve of pure samples

Figure 28 shows the DSC heating run for the pure components. It reveals melting ranges of 50-55°C and 55-61°C for the wax and EVA respectively. The melting peak of urea is centered at ca. 132°C. In the cooling run shown in Figure 29, urea shows a sharp crystallisation peak at 108°C. The wax and EVA show broader crystallisation exotherms at 55 and 57°C respectively.

The DSC curves for PVOH plasticised with glycerol were featureless in the temperature range 25–140°C. This suggests that the compound had an amorphous structure.

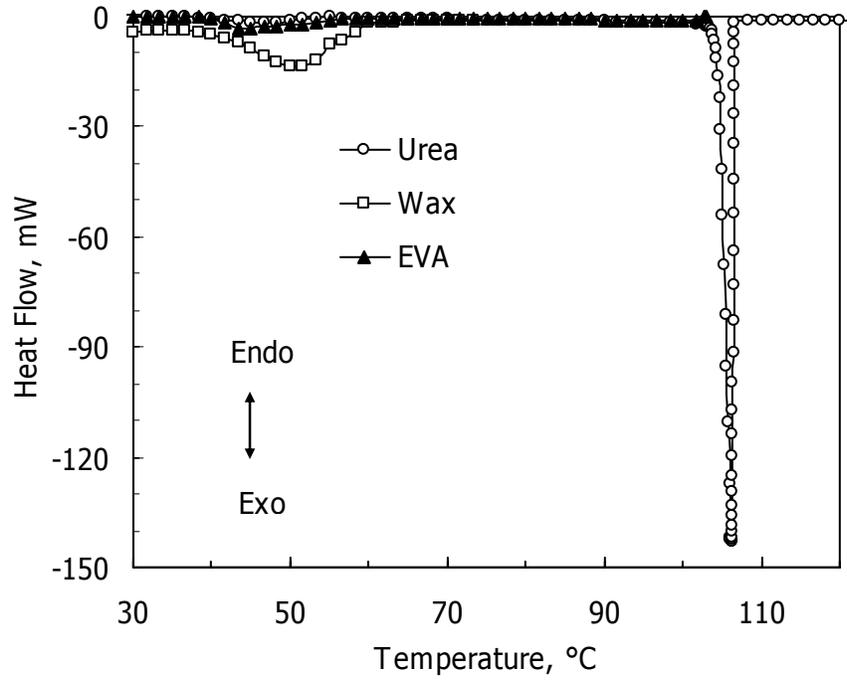
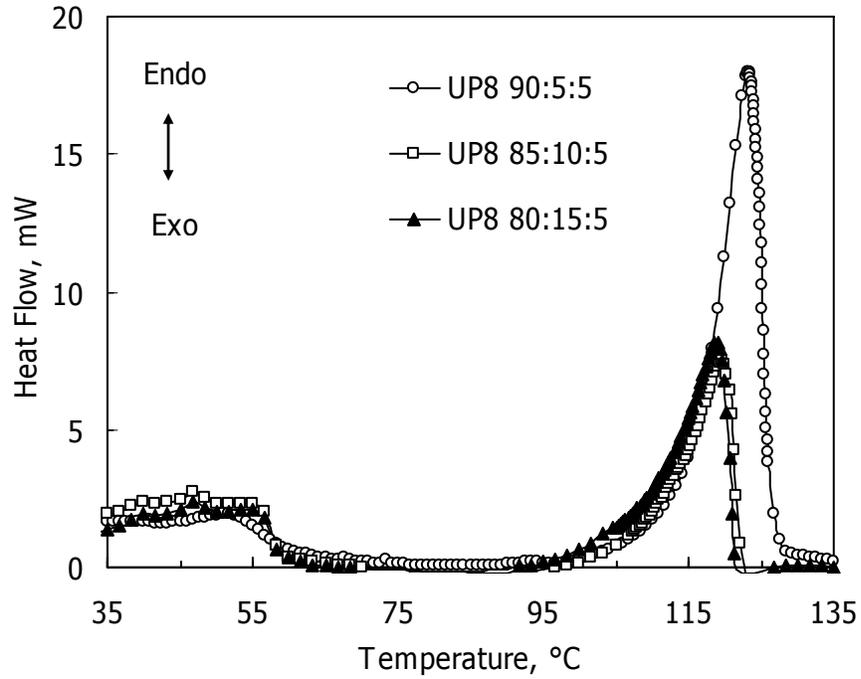
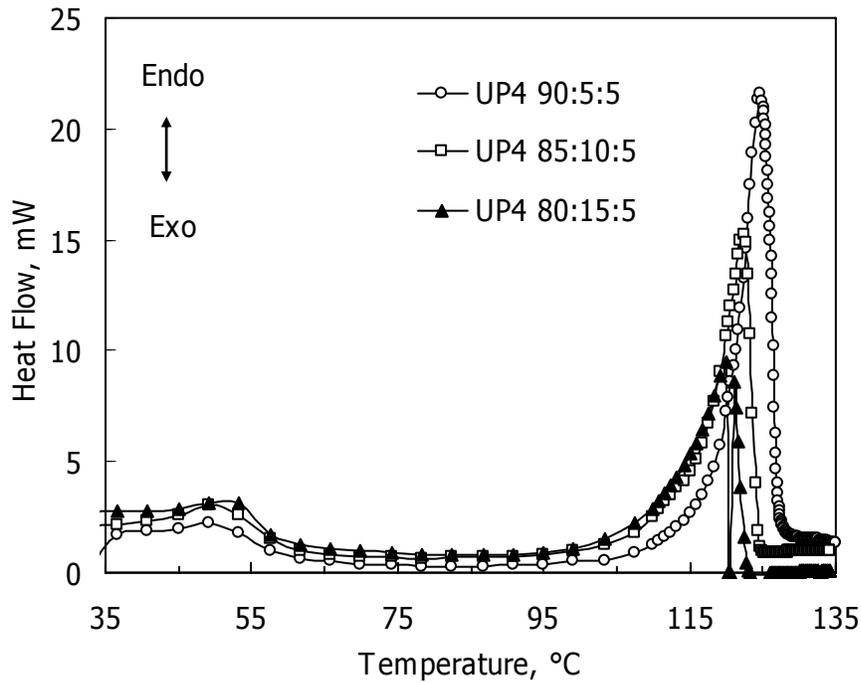


Figure 29: DSC cooling curve of pure samples

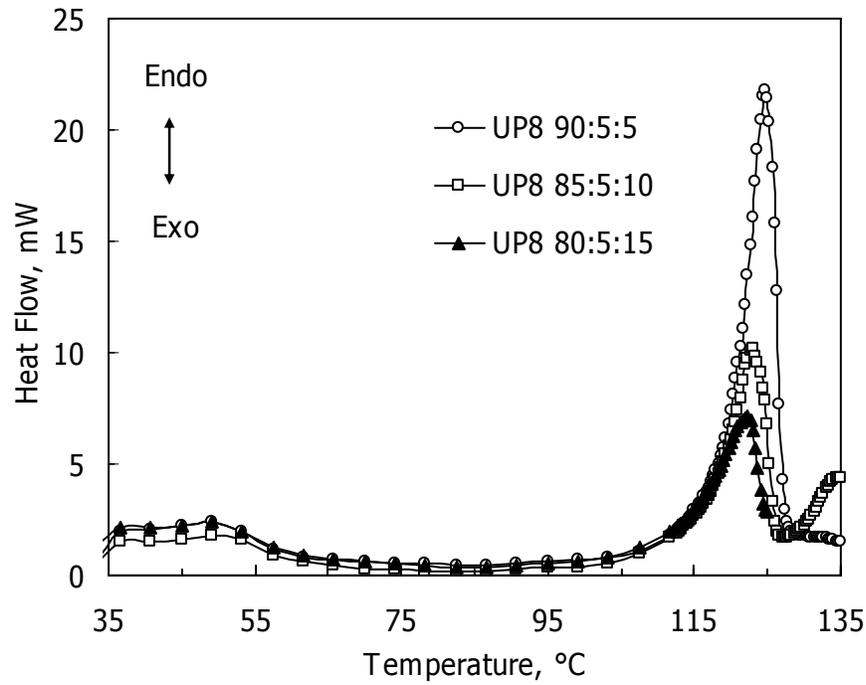


(a)

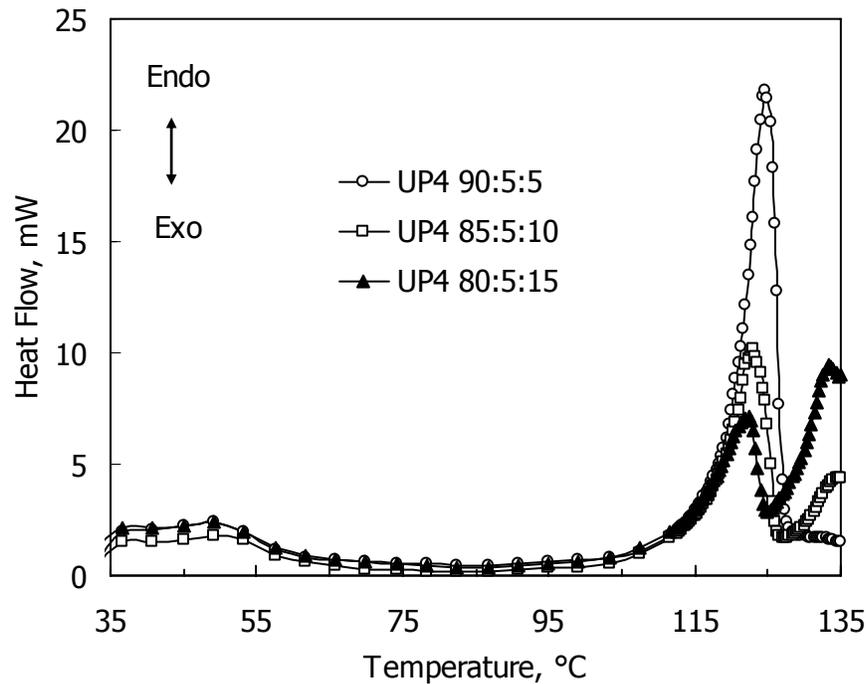


(b)

Figure 30: Effect of increasing the polymer content on the DSC heating curves of the PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and 40 phr



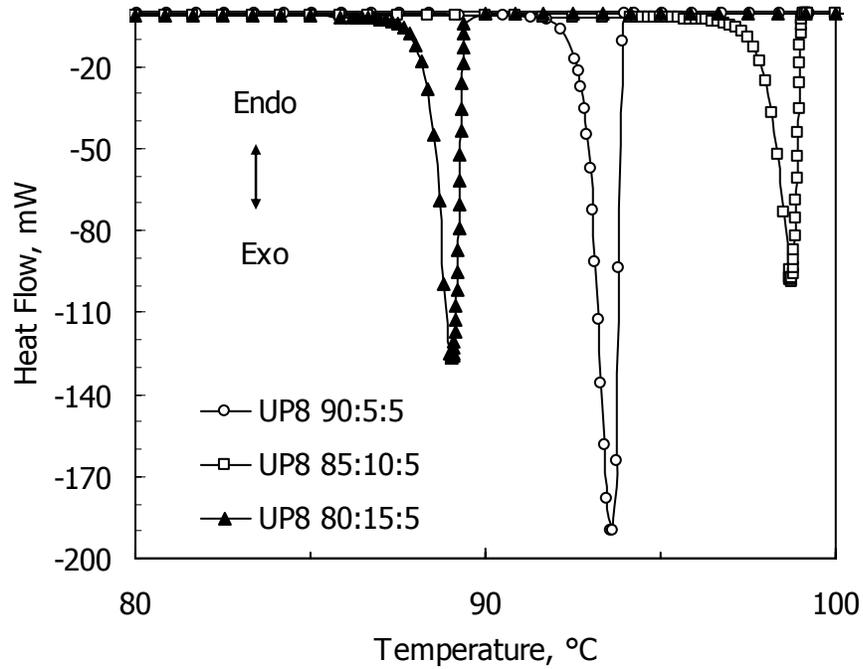
(a)



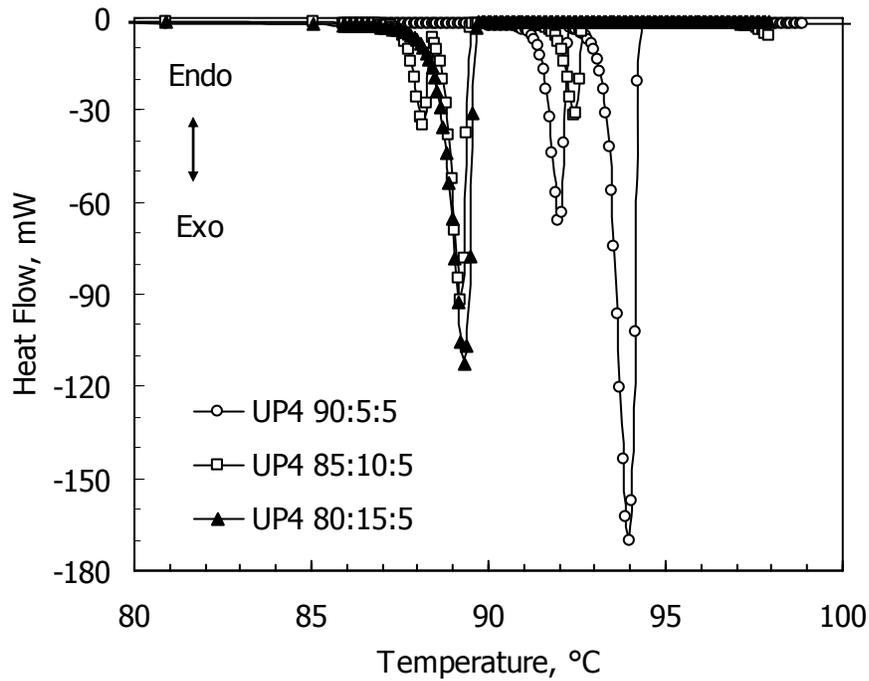
(b)

Figure 31: Effect of increasing the wax content on the DSC heating curves of the PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and (b) 40 phr

The effects of increasing the polymer and wax content on the thermal properties of PVOH moulding compounds are shown in Figures 30 and 31 and Table 12. At any degree of plasticisation, up to three endothermic peaks are observed in the heating curve and three exothermic peaks in the cooling curve. The endothermic peak centered at ca. 50°C is assumed to be the melting of the wax. The large endothermic peak at ca. 120°C is due to melting of the urea. The high-temperature endothermic peak, above the melting point of urea, is only observed at wax contents of 10% and 15%. It is not present when the wax content is 5%. Furthermore, the intensity of this peak increases with wax content. Therefore it is considered to be due to interaction of wax with urea, i.e. the formation of a wax-urea inclusion compound. The exothermic peaks observed in the cooling curve correspond to the crystallisation of these phases.

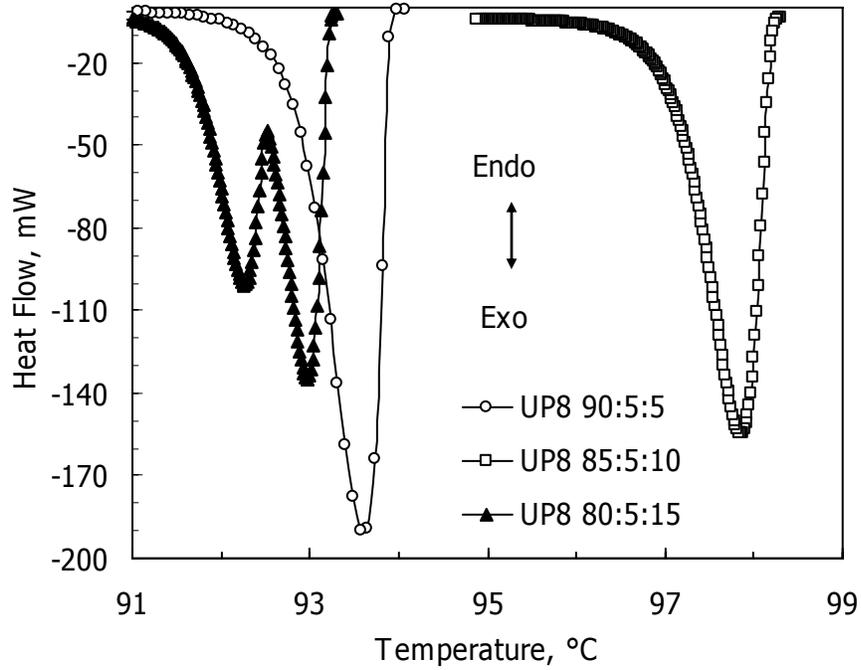


(a)

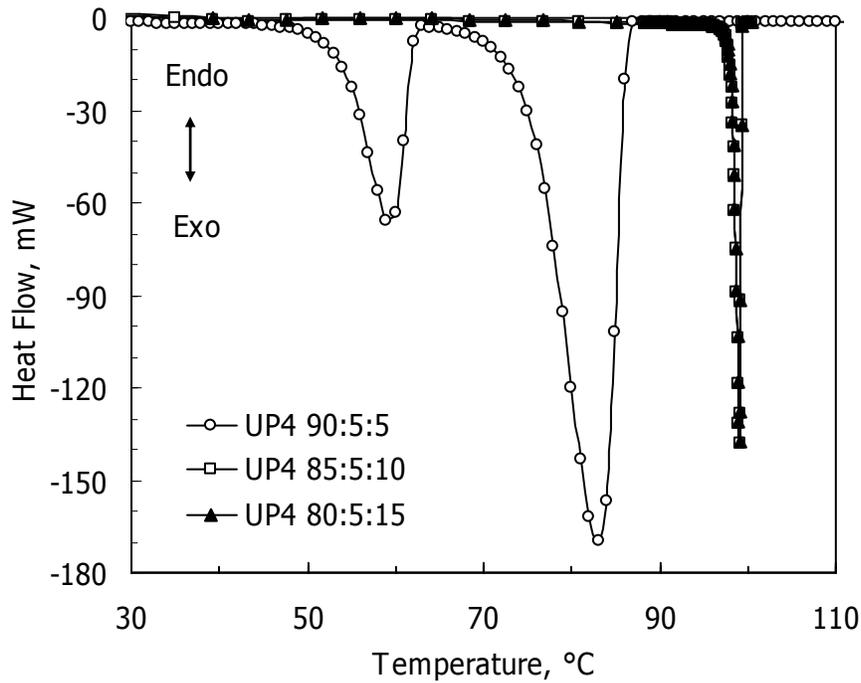


(b)

Figure 32: Effect of increasing the polymer content on the DSC cooling curves of the PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and (b) 40 phr



(a)



(b)

Figure 33: Effect of increasing the wax content on the DSC cooling curves of PVOH moulding compounds at plasticisation concentrations of (a) 80 phr and (b) 40 phr

The location of the cooling exothermic peak provides an indication of the ease of crystallisation of the compound. If large under-cooling is required before the compound crystallises, it implies that crystallisation is lethargic and that it will take a long time. Fast cycle times in injection moulding imply that rapid crystallisation is desired. Figure 32 (UP8 90:5:5 – UP8 80:15:5) shows the effect of PVOH content at a constant wax level of 5%. Note that the crystallisation occurs fastest at the intermediate PVOH content of 10%. The composition with 15% PVOH required the largest under-cooling before crystallisation commenced. Similar behaviour was shown by the UP4 compounds with the added complication that multiple crystallisation exotherms were found. The reason for this complex behaviour and non-linear composition-dependence is not understood at present. An explanation is beyond the scope of this technical investigation. Figure 33 (UP8 90:5:5 – UP8 80: 5: 15) shows the effect of wax content at a constant PVOH level of 5%. Here too crystallisation was fastest at the intermediate wax content of 10%. The composition with 15% wax showed multiple crystallisation exotherms. This could be due to the crystallisation of urea and a wax-urea clathrate. Non-homogeneity of the material owing to poor mixing or phase separation provides another possible explanation for the multiple crystallisation peaks.

Table 12: Parameters obtained from DSC measurements for investment casting patterns on the large-peak and pure samples

Sample	$T_{o,m}$	$T_m(^{\circ}C)$	$\Delta H_m (kJ/kg^{-1})$	$T_c(^{\circ}C)$	$T_{p,c}(^{\circ}C)$
Urea	125,9	130,2	147,2	108,1	106,2
Wax	43,4	53,4	105,1	56,2	53,3
UP8 90:5:5	116,3	120,1	103,3	96,2	93,6
UP8 85:10:5	111,3	120,7	79,6	100,3	98,7
UP8 80:15:5	112,3	119,1	68,9	89,3	88,9
UP8 80:5:10	114,1	121,1	51,1	97,2	96,5
UP8 80:5:15	121,5	122,3	35,3	92,3	88,6
UP4 90:5:5	122,5	125,3	102,6	93,1	89,6
UP4 80:10:5	118,1	121,1	89,3	87,2	88,7
UP4 80:15:5	116,2	120,9	72,5	82,1	81,6
UP4 80:5:10	117,3	120,9	52,8	96,6	94,1
UP4 80:5:15	118,2	123,1	39,1	96,8	94,9

Table 12 shows that, as expected, the enthalpy of melting decreases with an decrease in the urea content. This is not only because the content is reduced, but also because higher melting complexes of urea are also formed

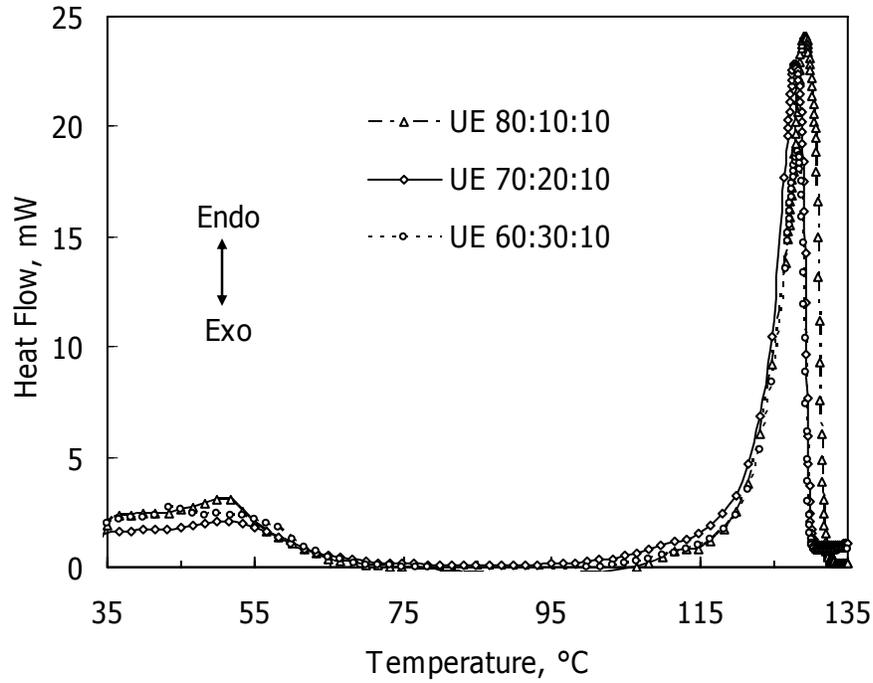


Figure 34: Effect of increasing the polymer content on the DSC heating curves of the EVA moulding compounds

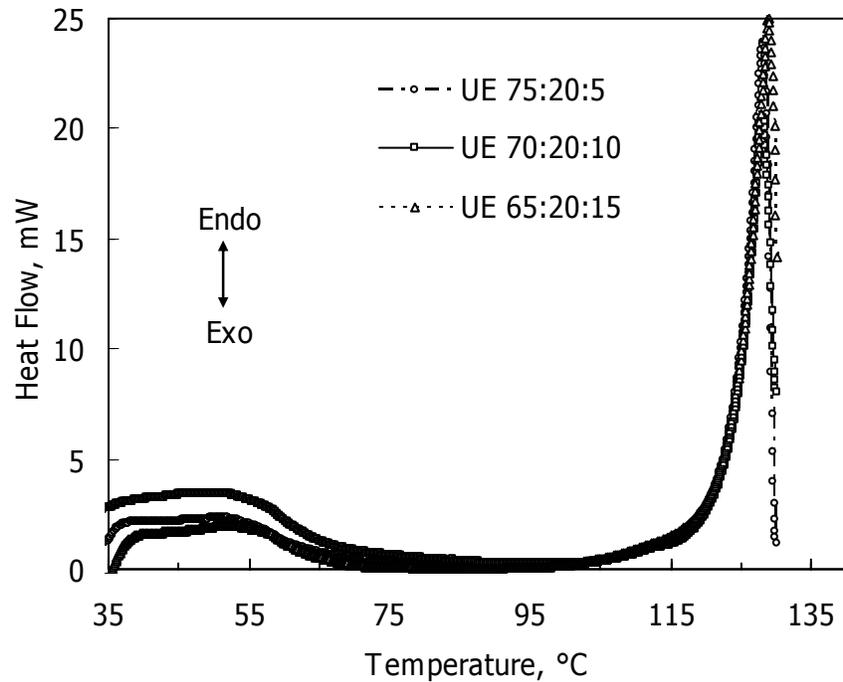


Figure 35: Effect of increasing the wax content on the DSC heating curves of the EVA moulding compounds

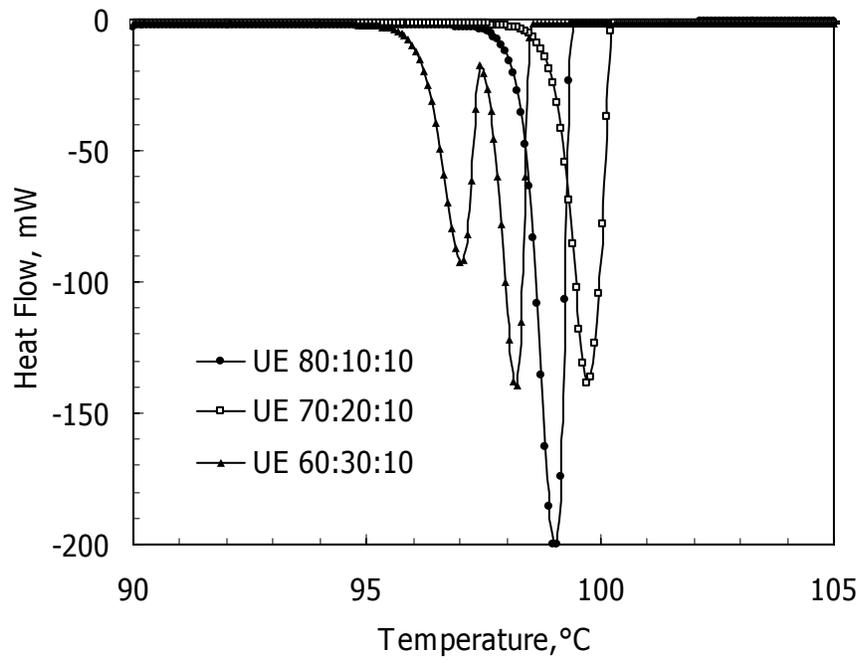


Figure 36: Effect of increasing the polymer content on the DSC cooling curves of the EVA moulding compounds

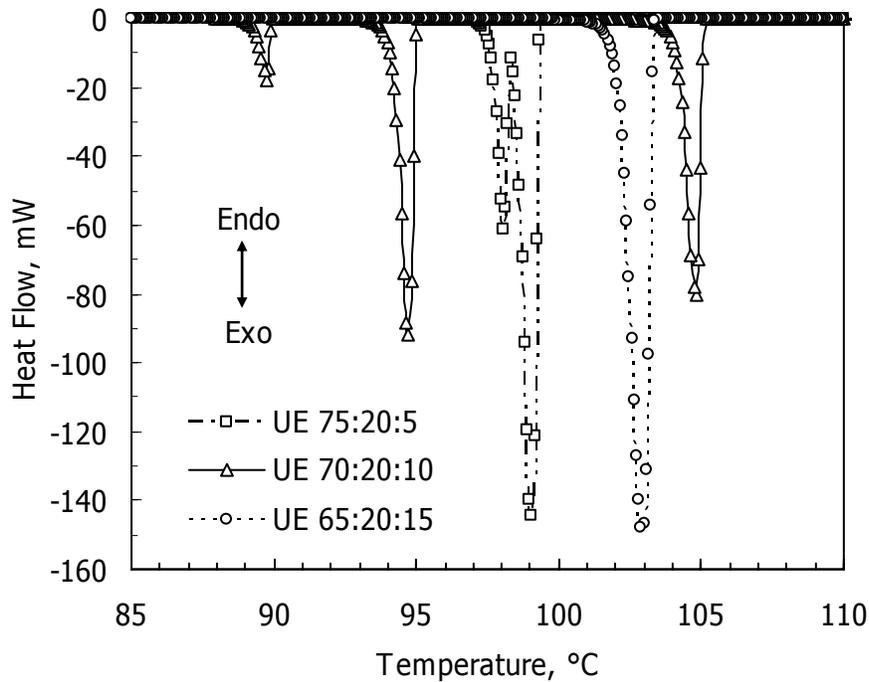


Figure 37: Effect of increasing the wax content on the DSC cooling curves of the EVA moulding compounds

Table 13: Properties obtained from differential thermal analysis of urea peak and EVA/wax blends

Sample	$T_{o,m}$ EVA/Wax Blend	ΔH_m (kJ/kg ⁻¹) EVA/Wax blend	$T_{o,m}$ Urea	Urea ΔH_m (kJ/kg ⁻¹)
EVA	59,3	15,2	-	-
UE 80:10:10	58,9	20,0	136,3	144
UE 70:20:5	59,0	24,4	135,2	131
UE 70:20:10	60,8	28,5	135,0	125
UE 65:20:15	62,9	30,9	135,9	133
UE 60:30:10	59,8	31,6	135,0	115

The effects of increasing the EVA and wax content on the thermal properties of EVA moulding compounds are shown in Figures 34 to 37 and Table 13. The results show two endothermic peaks and multiple exothermic peaks respectively. The small lower melting peak at ca. 60°C corresponds to the EVA and wax present in the blend. The EVA resin melts at 60-62°C and freezes at 62°C. The EVA freezes at the same temperature as paraffin wax. These two components co-crystallise, which allows the EVA resin to reinforce the wax. In the melt the wax acts as an internal lubricant as it interacts and dissolves in the polymer (EVA).

The large melting endotherm at ca. 133°C is due to urea. The melting of the urea occurs at higher temperatures than in the PVOH compounds. This could be due to the poor compatibility of the EVA and wax with urea: the low melt solubility leads to lesser melting point depression. This could explain why an increase in wax or EVA content does not affect the melting peak position as shown in Figures 34 and 35.

The effects of increasing the polymer and wax content on the cooling curve exotherm are shown in Figures 36 and 37. There is no consistent trend to explain the effect of the wax or polymer. Multiple exothermic peaks are more pronounced at high wax content (15%) at a constant polymer content of 20%. This could be due to the formation of inclusion compounds with different crystallisation behaviours. The possibility also exists that the material is inhomogeneous due to poor mixing.

As shown in Table 13, an increase in either the wax or EVA content increases the heat of melting and the EVA/wax peak increases. The increment is less significant in the case of EVA and could be explained by its amorphous nature. The peak of the heat of melting of urea decreases with an increase of either wax or EVA.

The melting and multiple crystallisation temperatures of PVOH moulding compounds are slightly lower compared with EVA moulding compound. The industrial cooked urea-based compound presented the lowest melting temperature at ca. 107°C this is shown in Appendix E. This could be explained by the fact that PVOH reacts with molten urea, forming urethane compounds with lower melting points.

8.2.2 Vicat softening temperature

Vicat softening is a comparative technique that provides an indication of the relative softness of a material. It is a standardised test method described by ASTM 1525 and ISO 306. It is determined as the temperature at which, under a specified load (in the present study), a flat-ended needle enters to a depth of 1 mm.

In this study the Vicat softening temperature of the urea-based compounds was compared with that of the cooked urea formulation. Materials with a higher Vicat softening point are expected to offer enhanced property retention at elevated temperatures. This has obvious implications for storing, handling and transporting conditions.

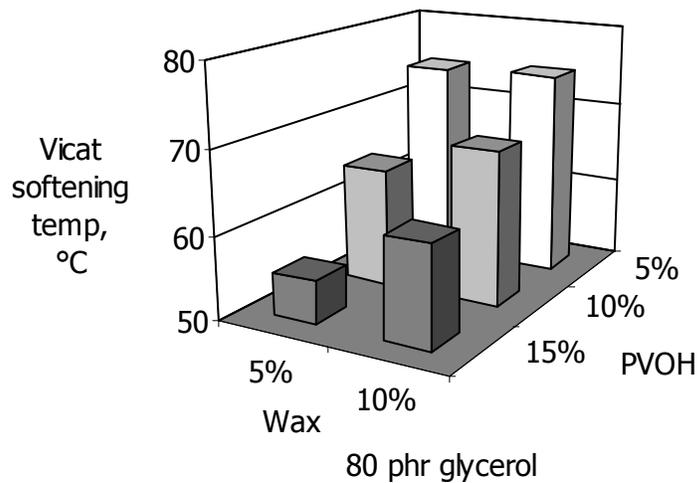


Figure 38: Softening temperature of the PVOH (80 phr glycerol) moulding compounds

Figure 38 shows that the softening temperature increases with an increase in the wax and a decrease in the polymer content. The current PVOH compounds had higher softening temperatures than the cooked urea moulding compound (benchmark) which shows are hardness.

8.3 Mechanical properties

8.3.1 Charpy impact test

Impact testing is a mechanical procedure used to check the ability of a material or an object to withstand a high loading rate. This is quantified as the energy or the force required to fracture the sample.

Experimental data analysis design (two-way ANOVA Charpy impact test)

There is always anxiety about the analysis of data generated from an experiment. It is important to take time and effort to arrange the experiment correctly to guarantee that the data

obtained is adequate to respond to questions of concern as clearly and efficiently as possible. In this study factorial experimental designs were used. In such designs the effects of more than one factor on a given response variable are considered. Factorial experimental designs allow the effect of a factor on the response variable to be determined and also whether separate factors may have a mutual effect.

To this end a linear model is postulated and analysis of variance (ANOVA) is used to test for the significance of the factors. Two-way ANOVA is a way of studying the effects of two factors separately, e.g. the direct effects of the wax and polymer contents, and of the wax and polymers together (the interaction effect). The advantage of factorial designs over single factorial experiments is that they are more efficient and they allow interactions to be detected. The two-way ANOVA approach is illustrated here using the experimental data obtained from the Charpy impact test and the three-point bending test (flexural strain, flexural stress, modulus of elasticity, work done) for the EVA and PVOH urea-based moulding compounds. A systematic example of how the two-way ANOVA was carried out is shown in the case of Charpy impact test. The same technique is applied for the three-point bending experimental data results.

The pattern moulding compound has two defining composition characteristics, namely the wax and polymer additive levels. It is reasonable to ask whether a performance property, e.g. the Charpy impact strength, varies with the polymer and wax contents. Thus these levels can be regarded as two predictors that may explain differences in measured Charpy impact strengths. There could be an overall difference in Charpy impact strength due to a difference in the polymer content. There is possibly a difference in the Charpy impact strength due to differences in wax content (irrespective of the polymer). These effects are called "additive".

Two-way ANOVA was used to find out whether the physical property data of the moulding compound is affected by the presence of the wax and polymer additives. In effect, two-way ANOVA checks whether data from two groups have a common mean. One-way ANOVA and two-way ANOVA differ in that the groups in two-way ANOVA have two categories that may define several performance characteristics instead of one.

Finally, there could be synergy or antagonism in a physical property due to interactions between the additives. Such interaction effects are impossible to detect unless there are duplicate observations for at least some combinations of the additives. Two-way ANOVA is a special case of the linear model and its form is defined as follows:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk} \quad (30)$$

The subscripts in this model have the following meaning: with row index i , column index j , and repetition index k . Here y_{ijk} is a matrix of observations, e.g. Charpy impact strength. The quantity μ denotes the overall mean Charpy impact strength. α_i is a matrix whose columns are the deviations of each compound's Charpy impact strength (from the mean Charpy impact strength) which are attributable to the wax concentration used. All values in a given column of α_i are identical, and the values in each row of α_i sum to 0. β_j is a matrix whose rows are the deviations of Charpy impact strength (from the mean Charpy impact strength) which are attributable to the polymer concentration used. All values in a given row of β_j are identical, and the values in each column of β_j sum to 0. γ_{ij} is a matrix of interactions. The values in each row of γ_{ij} sum to 0, and the values in each column of γ_{ij} sum to 0. ε_{ijk} is a matrix of random errors or "disturbances". F statistics are used to do hypothesis tests to find out whether a physical property value is the same across all additive 1 levels, additive 2 levels and additive1-additive 2 pairs (after adjusting for the "additive" effects).

The impact strength data was subjected to ANOVA using the Matlab script files ImpactUP8, ImpactUP4 and ImpactEVA for the PVOH- and EVA-based moulding compounds respectively. This is shown in Appendix G. The natural logarithm of the Charpy values was chosen as the response variable. The output obtained from running this script file is shown in Tables 14 to 16 below. It presents a two-way ANOVA for Charpy impact strength data. Matlab's function ANOVA2 returns the p-values from these tests. These values assume that the random disturbances ε_{ijk} in the model equation are independent and normally distributed with constant variance. The linear regression model equations are also used to fit the model; these are shown in equations 31 to 33 below. The experimental data and the predicted data are then compared to establish a fit as shown in Figures 39 to 41 below.

Table 14: Two-way ANOVA for Charpy impact strength for the urea-PVOH-wax compound containing 80 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	6,86	2	3,43	62,53	< 0,0001
PVOH	20,38	2	10,19	185,64	< 0,0001
Wax * PVOH	0,18	4	0,0457	0,83	0,5135
Error	1,98	36	0,0549		
<i>Total</i>	<i>29,40</i>	<i>44</i>			

F is the F statistic

Table 15: Two-way ANOVA for Charpy impact strength for the urea-PVOH-wax compound containing 40 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	0,385	2	0,1924	5,39	0,0090
PVOH	6,244	2	3,1219	87,44	< 0,0001
Wax * PVOH	0,615	4	0,1537	4,3	0,0060
Error	1,285	36	0,0357		
<i>Total</i>	<i>8,529</i>	<i>44</i>			

Table 16: Two-way ANOVA for Charpy impact strength for the urea-EVA-wax compounds

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	4,866	2	2,4330	44,77	< 0,0001
PVOH	21,221	5	5,3052	97,62	< 0,0001
Wax * EVA	0,032	4	0,0107	0,2	0,8981
Error	2,174	40	0,0544		
<i>Total</i>	<i>28,293</i>	<i>49</i>			

Linear regression was performed using the Matlab regress function and the script files ImpactUP8Linear, ImpactUP4Linear and ImpactEVALinear for the PVOH- and EVA-based moulding compounds respectively. This is shown in Appendix G. Linear regression yielded the following equations:

PVOH (80 phr glycerol):

$$Y_{Charpy} = \exp(-0,2604 - 9,540 X_{wax} + 16,339 X_{PVOH}) \quad (r^2 = 0,9133) \quad (31)$$

PVOH (40 phr glycerol):

$$Y_{Charpy} = \exp(-0,4416 - 5,272 X_{wax} + 5,491 X_{PVOH} + 36,32 X_{wax}X_{PVOH}) \quad (r^2 = 0,715) \quad (32)$$

Urea-EVA-wax:

$$Y_{Charpy} = \exp(-2,059 + 2,411 X_{wax} + 11,50 X_{EVA}) \quad (r^2 = 0,991) \quad (33)$$

The predictions are compared against the experimental data in Figures 38 to 40.

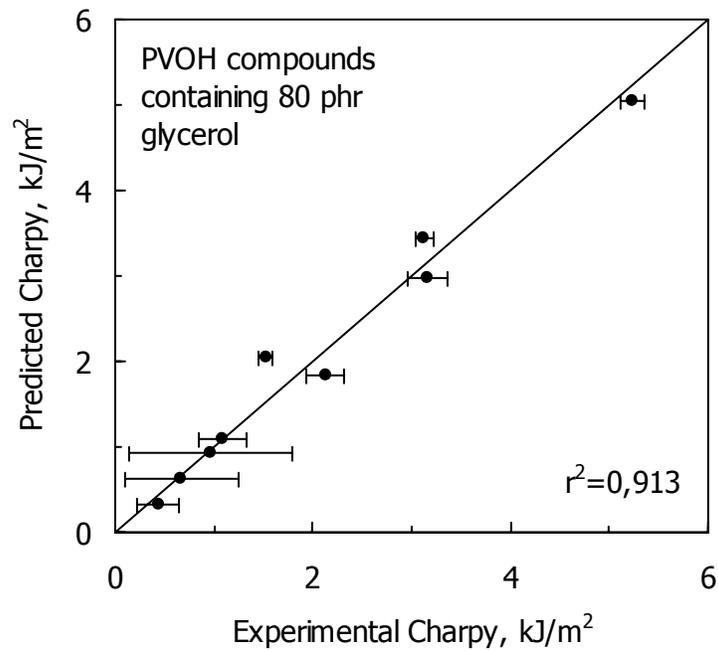


Figure 39: Comparison between predicted and experimental Charpy impact strength for quadratic model fit of the urea-wax-PVOH (80 phr glycerol) compounds

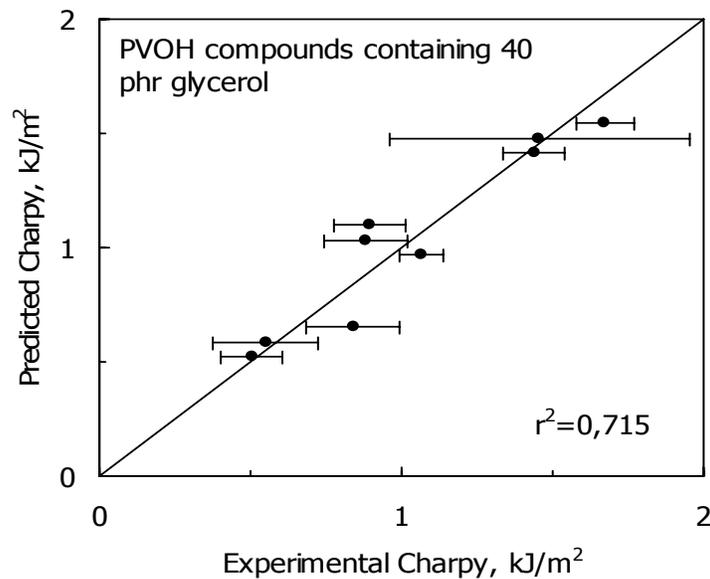


Figure 40: Comparison between predicted and experimental Charpy impact strength for quadratic model fit of the urea-wax-PVOH (40 phr glycerol) compounds

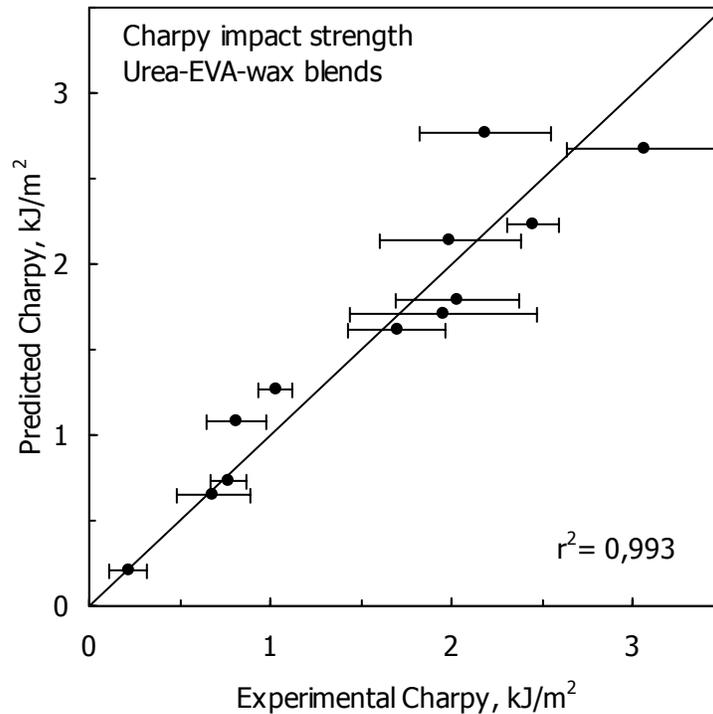


Figure 41: Comparison between predicted and experimental Charpy impact strength for linear model fit of the urea-EVA-wax compounds

Data analysis

The two-way ANOVA results for the PVOH urea-based moulding compounds containing 80 phr and 40 phr glycerol, and for the EVA moulding compounds are shown in Tables 14 to 16.

It is concluded that the polymer and wax contents and their interaction are significant in all three cases. The experimental average impact test results are shown in Figures 42 to 44. In the case of the EVA and urea-wax-PVOH (80 phr glycerol) moulding compounds, the model fits, with over 91% of the total variation in the data about the average explained. A poor fit, with only 78% of the total variation in the data about the average explained, was shown by the urea-wax-PVOH (40 phr) moulding compound. The average results of the data analysed are depicted in Figures 41 to 43 below.

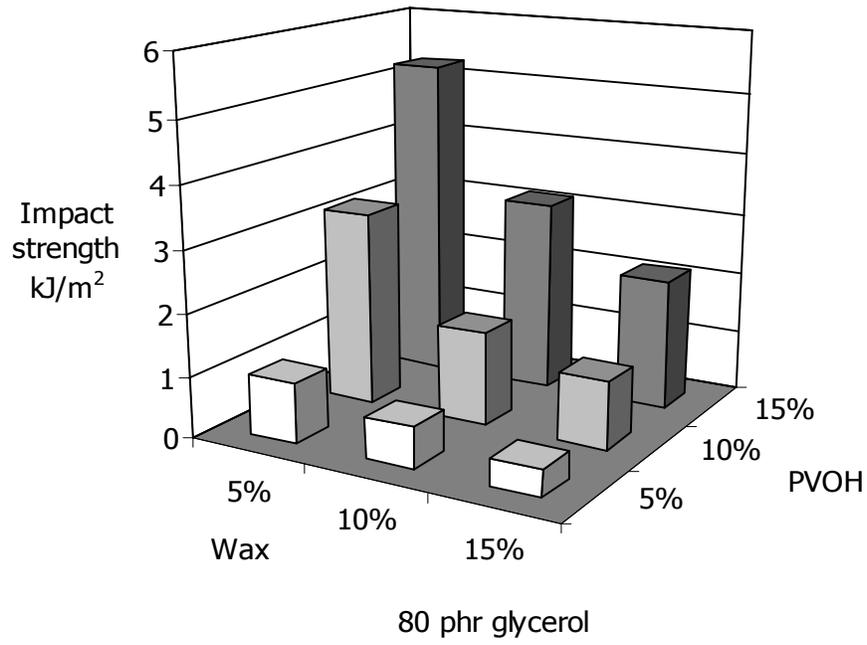


Figure 42: Charpy impact strength of the urea-wax-PVOH (80 phr glycerol) compounds

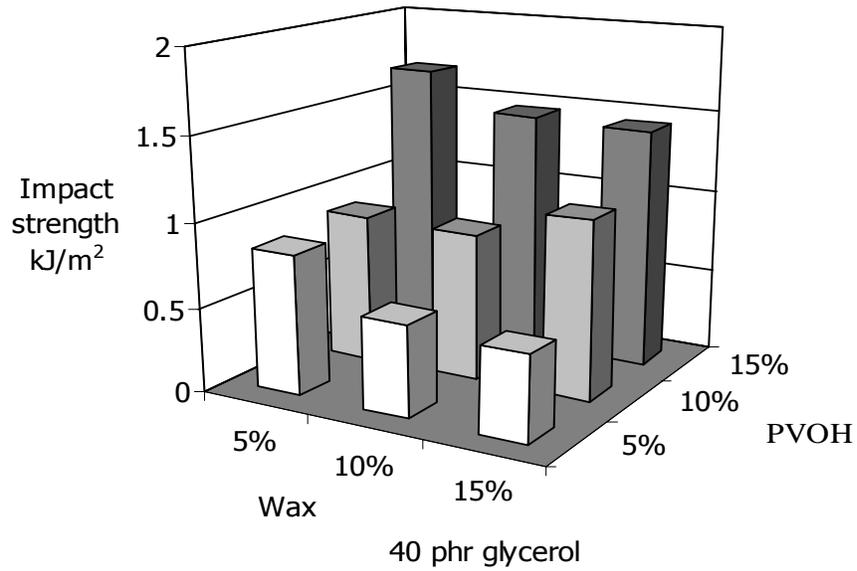


Figure 43: Charpy impact strength of the urea-wax-PVOH (40 phr glycerol) compounds

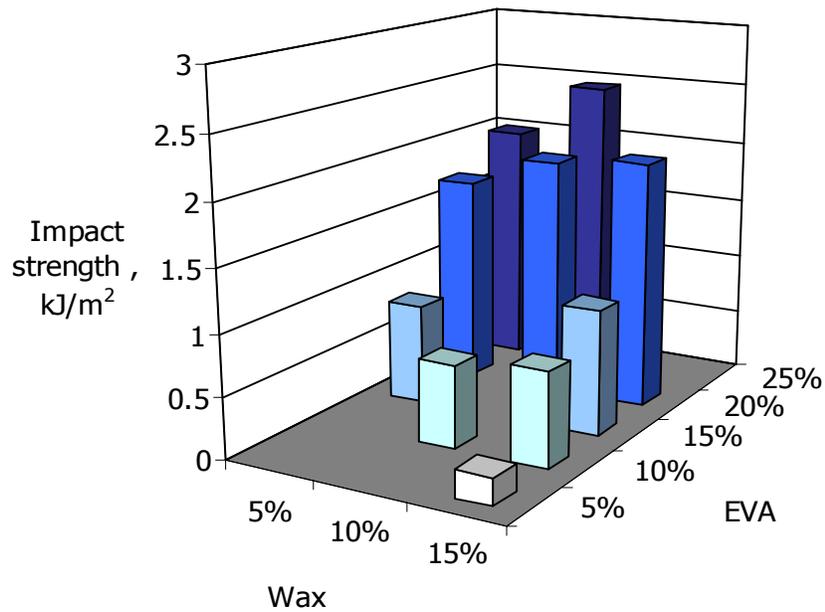


Figure 44: Charpy impact strength of the urea-EVA-wax compounds

The results given in Figures 42 and 43 shows that the impact strength increases as the PVOH content is increased, as is expected at any degree of plasticisation. An increase in the wax content affects the break results to a very small extent at any degree of plasticisation. This is because PVOH is highly hydrophilic, wax is hydrophobic and there seems to be no interaction between them.

An increase in the degree of plasticisation from 40 to 80 (per hundred resin) phr improves the impact strength. This is attributed to the lowering of the glass transition temperature (T_g) of the PVOH binder as the amount of plasticiser is increased. The net effect is an increase in the flexibility and elongation to break of the binder.

As expected, Figure 44 shows that the impact strength increases with EVA content. Adding wax provides a marginal improvement. This is attributed to the compatibility of the wax-EVA blend. The Charpy impact strength data show that the PVOH-urea moulding compound is seven times tougher than the EVA-urea compound. This difference could be due to urea-polymer interactions: urea has the ability to form strong hydrogen bonds with the hydroxyl groups of PVOH. In the case of the EVA moulding compounds, the acetate group is expected to interact more weakly with the urea. A second factor is the difference in molecular masses: the PVOH had a much higher molecular mass than the EVA. It is well known that polymer properties improve with molecular mass. Lastly, the PVOH moulding compounds have a superior impact strength compared with the industrial cooked urea moulding compound. This is because part of the urea might have degraded at the high processing temperatures used in the cooking process.

8.3.2 Three-point bending test

The three-point bending test measures the flexural stress-strain response of the material. From such curves one can determine values for the modulus of elasticity in bending, the flexural stress and the flexural strain. The main advantage of a three-point flexural test is that it can be used to characterise very brittle material such as that being studied here. Additional advantages include the ease of the specimen preparation and testing. Sample of ceramics cannot be “gripped” in the same way as normal strength test. This is another use for 3 point bend test.

Load deflection curves

The load deflection curves are the raw data obtained from the flexural test that gives an indication of the toughness and strength of the moulding compound. Using load and deflection values, the flexural strain and stress are calculated from the standard equations described in equation 7 and 8 in the literature study using ASTM D70. The load deflection curves are also used to calculate the modulus of elasticity. This is done by calculating the steepest slope under load deflection curve and using equation 9 in the literature. Fracture energy is calculated as the area under the load deflection curve.

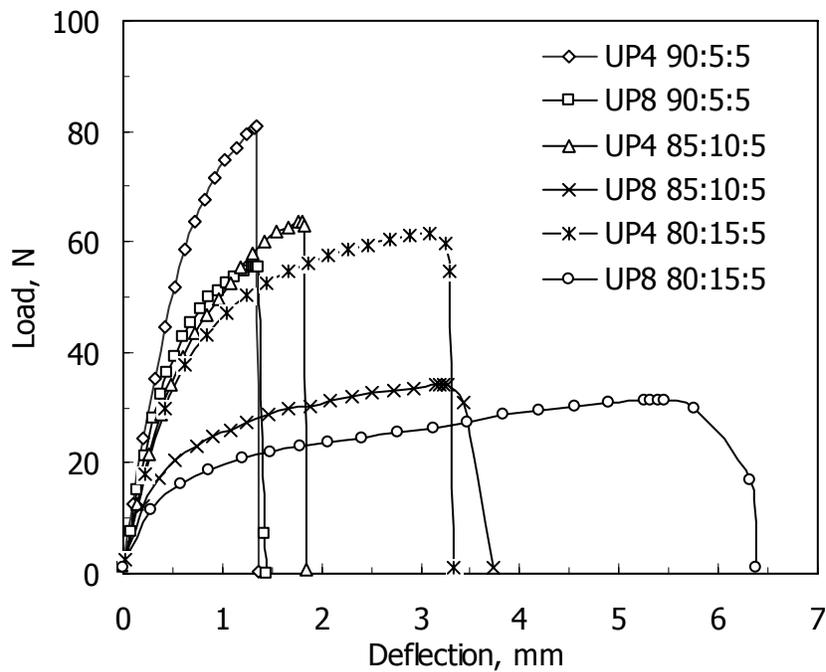


Figure 45: Load deflection curve showing the effect of increasing the PVOH content on the mechanical properties of the urea-PVOH-based compounds

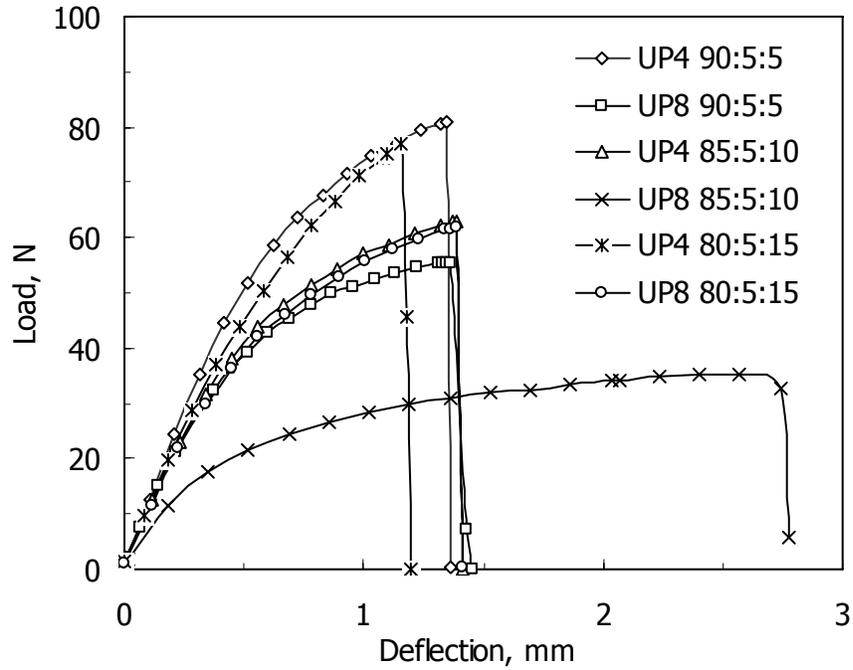


Figure 46: Load deflection curve showing the effect of increasing the wax content on the mechanical properties of the urea-PVOH-based compounds

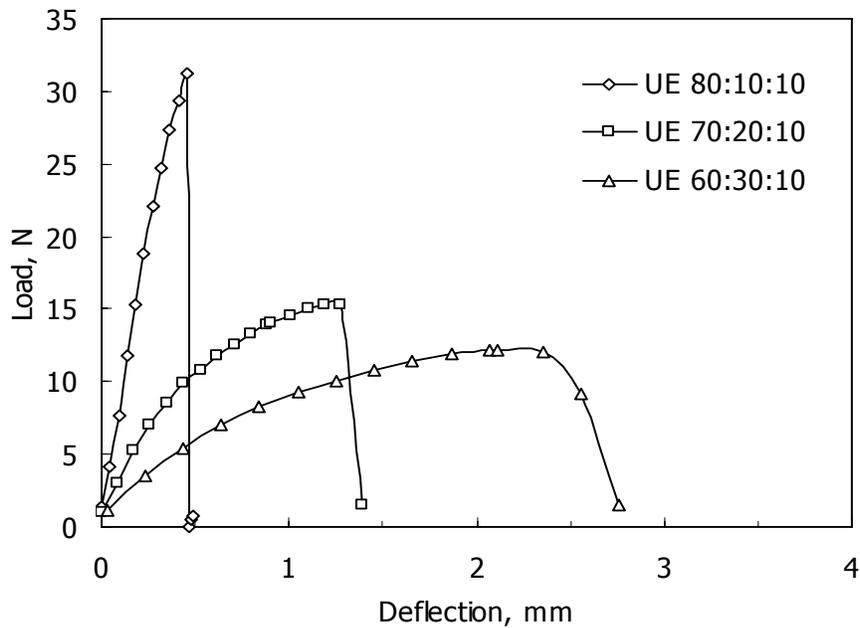


Figure 47: Effect of varying EVA content on the load deflection curve of the EVA moulding compounds

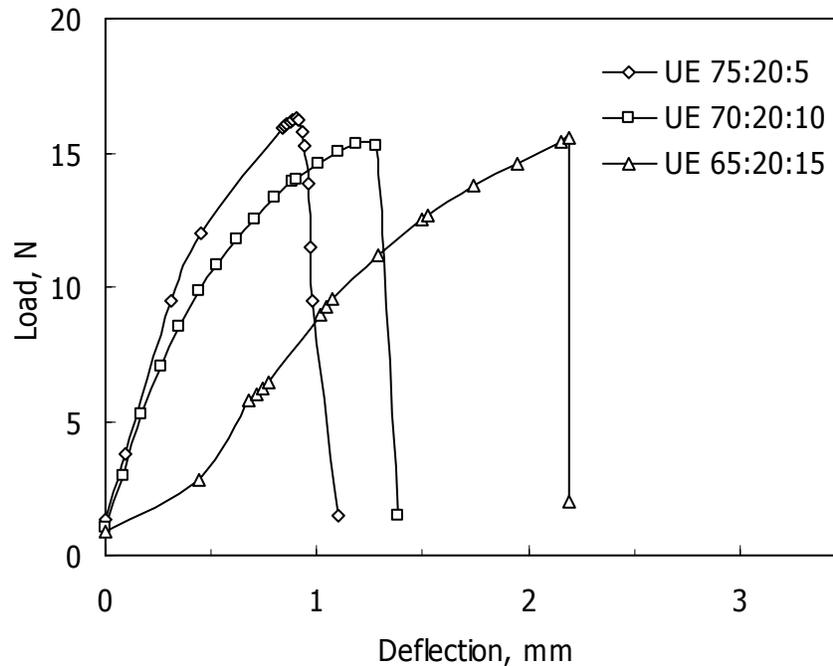


Figure 48: Effect of varying wax content on the load deflection curve of the EVA moulding compounds

The effect on the EVA and PVOH moulding compounds of increasing the wax and polymer contents was studied using load deflection curves. In the case of the PVOH moulding compounds, the effect of increasing the wax content from 5% to 15% at a constant PVOH content of 5% was studied. For the EVA moulding compound, the effect of increasing the polymer content at a constant wax content of 10% was studied. Lastly, the effect of increasing the wax content from 5% to 15% at a constant polymer content of 20% was studied.

As shown in Figure 45, a decrease in the PVOH content increases the maximum load and reduces the deflection to failure. This makes the moulding compounds strong but less tough i.e. change from ductile to brittle failure. This is because urea increases the stiffness in the polymer-filler matrix. This is seen at each degree of plasticisation. As shown in Figure 46, an increase in the wax content reduces the deflection to failure; this could be because the wax is crystalline and thus increases the stiffness.

As the degree of plasticisation (amount of glycerol) increases, the intermolecular friction between the PVOH molecules is reduced. This allows the molecules to slip and slide over each other more easily, thus reducing the rigidity of the PVOH and making it more flexible. An increase in the degree of plasticisation will therefore decrease the load at break (because there is less polymer) and increase the deflection at break.

As shown in Figure 47, as the EVA content is increased, the maximum load to failure decreases and the deflection increases. This produces moulding compounds that are less strong but tougher. This is because the increased EVA content provides greater flexibility and toughness.

As shown in Figure 48, an increase in the wax content does not affect maximum load but reduces the deflection. This polymer-filler interaction produces patterns that are strong but not tough.

Table 17: Maximum Load and deflection point of PVOH moulding compounds

Urea:PVOH:wax	Maximum load (N)	Maximum Deflection (mm)
90:5:5	79,6± 2,2	1,40± 0,12
85:10:5	61,7± 1,9	2,22± 0,36
80:15:5	60,8± 1,9	3,56± 0,13
85:5:10	81,6± 5,5	1,55 ± 0,27
80:5:15	81,2± 3,6	1,37 ± 0,28

Table 18: Maximum Load and deflection point of EVA moulding compounds

Urea:EVA:wax	Maximum load (N)	Maximum Deflection (mm)
75:20:5	16,8± 0,3	0,90± 0,06
80:10:10	29,9± 1,6	0,54± 0,02
70:20:10	21,2± 0,3	1,17± 0,09
60:30:10	11,6± 0,15	2,25± 0,03
65:20:15	17,1± 0,4	2,86±0,10

PVOH urea-based moulding compounds, on average, have loads-at-break several times greater than EVA-urea-based compounds. This is shown in Table 17 and 18. The deflection results show that the PVOH urea-based moulding compounds deflect less easily than the EVA-urea-based compounds. The type of polymer–filler interaction could explain this. In the case of the PVOH moulding compounds, there are strong hydrogen bonds between the OH group and the highly hydrophilic urea molecule, whereas in the case of the EVA moulding compounds there is weaker interaction between the acetate group and the urea molecules.

PVOH moulding compounds has superior mechanical properties compared with cooked PVOH moulding compound. This could be due to the breakdown of the compound as it is cooked above the urea degradation temperature of 132°C.

Flexural stress

Flexural strength is also known as modulus of rupture, bending strength or fracture strength. The strength of a material in bending is expressed as the tensile stress on the outermost side of a bent test specimen, at the instant of failure. In flexural bending the sample is both in compression and tension. This is important as materials can fail in both tension and compression. This parameter determines the strength of a moulding compound to prevent any breakage during the assembly process of investment casting. The two-way ANOVA results obtained from the flexural stress experimental data are shown in Tables 19 to 21 below. The experimental data and the predicted data (linear regressed data) are then compared to establish a fit. The regression equations and the figures (Figures 49 to 51) are shown below.

Table 19: Two-way ANOVA for flexural stress data for the urea-wax-PVOH compound containing 80 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	11,55	2	5,78	2,99	<0,0001
PVOH	2571,58	2	1285,79	665,84	<0,0001
Wax * PVOH	47,07	4	11,77	6,09	<0,0001
Error	69,72	36	1,93		
<i>Total</i>	<i>2699,72</i>	<i>44</i>			

Table 20: Two-way ANOVA for flexural stress data for the urea-wax-PVOH compound containing 40 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	64,13	2	32,07	10,28	<0,0001
PVOH	2335,95	2	1167,98	374,56	<0,0001
Wax * PVOH	222,63	4	55,66	17,85	<0,0001
Error	112,26	36	3,12		
<i>Total</i>	<i>2734,97</i>	<i>44</i>			

Table 21: Two-way ANOVA for flexural stress data for the urea-EVA-wax compounds

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	115,45	2	57,725	164,09	<0,0001
EVA	822,12	5	164,425	467,38	<0,0001
Wax * EVA	64,76	4	16,191	46,02	<0,0001
Error	16,89	48	0,352		
<i>Total</i>	<i>1019,22</i>	<i>59</i>			

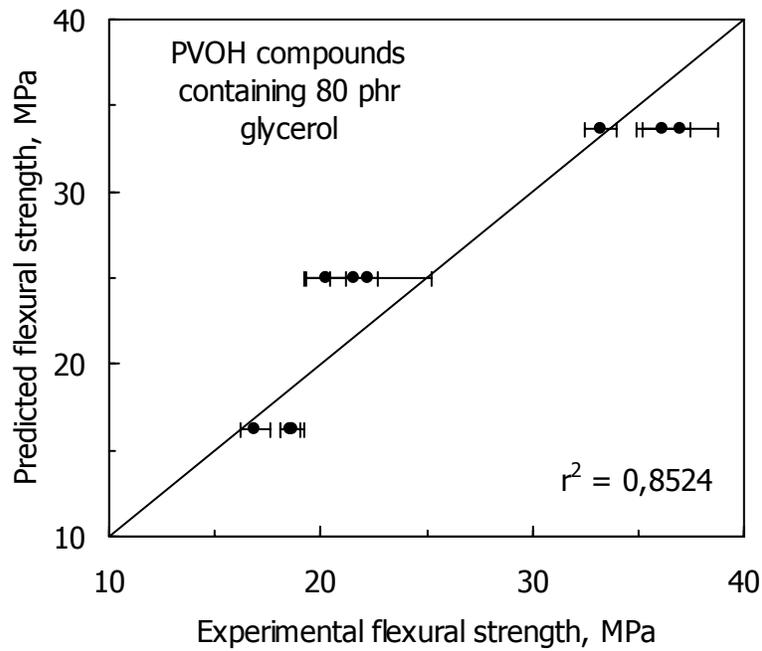


Figure 49: Comparison between predicted and experimental flexural stress data for linear model fit of the urea-wax-PVOH (80 phr glycerol) compound

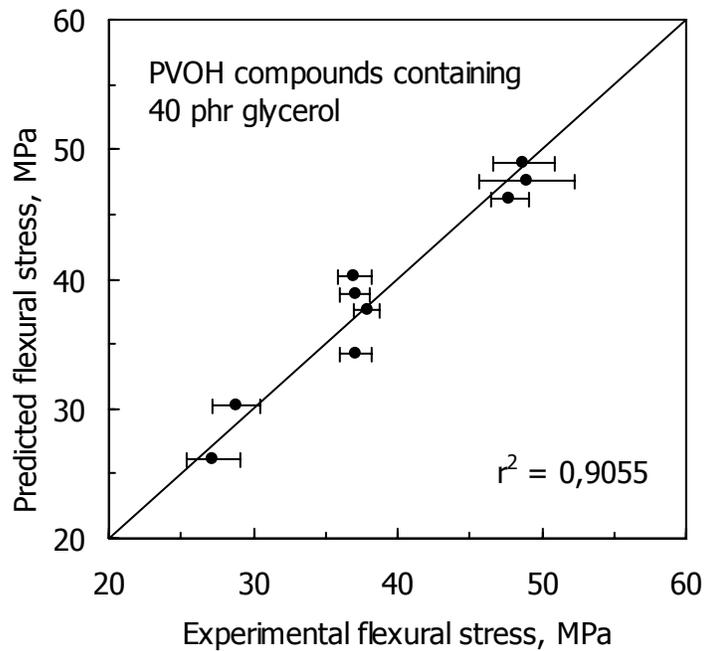


Figure 50: Comparison between predicted and experimental flexural stress for a linear model fit of UP4 data

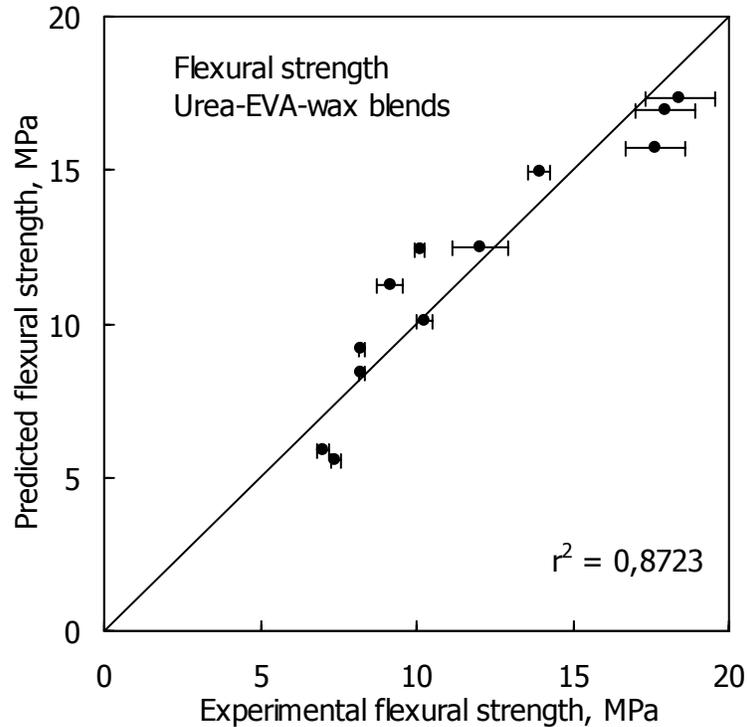


Figure 51: Comparison between predicted and experimental flexural stress for linear model fit of urea EVA-wax data

Data analysis

The two-way ANOVA result for the PVOH urea-based moulding compounds containing 80 phr and 40 phr glycerol, and the EVA compounds are shown in Tables 19 to 21. It is concluded that the polymer, the wax and their interaction are significant in all three cases. The regression yields:

PVOH (80 phr glycerol):

$$Y_{Flexural\ stress} = 38,17 + 42,10 X_{wax} - 143,95 X_{PVOH} - 303,80 X_{wax} X_{PVOH} \quad (r^2 = 0,8512) \quad (34)$$

PVOH (40 phr glycerol):

$$Y_{Flexural\ stress} = 48,2 - 65,9 X_{wax} + 81,4 X_{PVOH} - 1083,1 X_{wax} X_{PVOH} \quad (r^2 = 0,7714) \quad (35)$$

Urea-EVA-wax:

$$Y_{Flexural\ stress} = 28,40 - 73,91 X_{wax} - 57,60 X_{EVA} + 170,94 X_{wax} X_{EVA} \quad (r^2 = 0,8723) \quad (36)$$

In the case of the EVA and urea-wax-PVOH (80 phr glycerol), the model fits with over 85% of the total variation in the data about the average explained. A poor fit with only 77% total variation in the data about the average explained was shown by the urea-wax-PVOH (40 phr) moulding compounds. The average results of the data analysed are depicted in Figures 52 to 54 below.

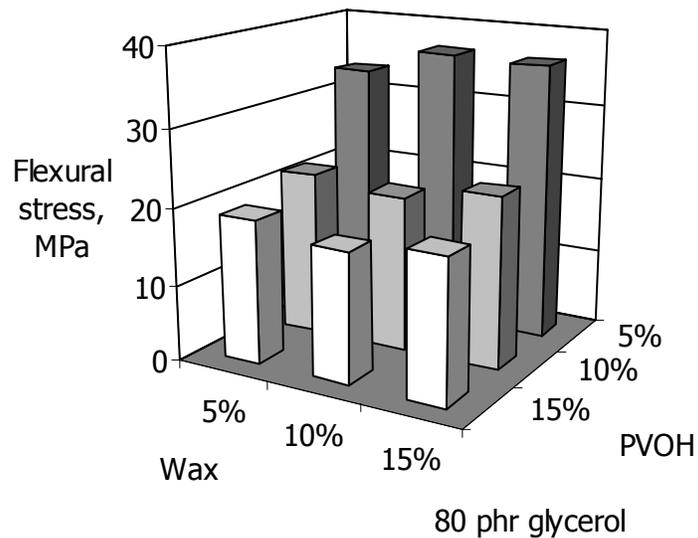


Figure 52: Flexural stress of the urea-wax-PVOH (80 phr glycerol) compound

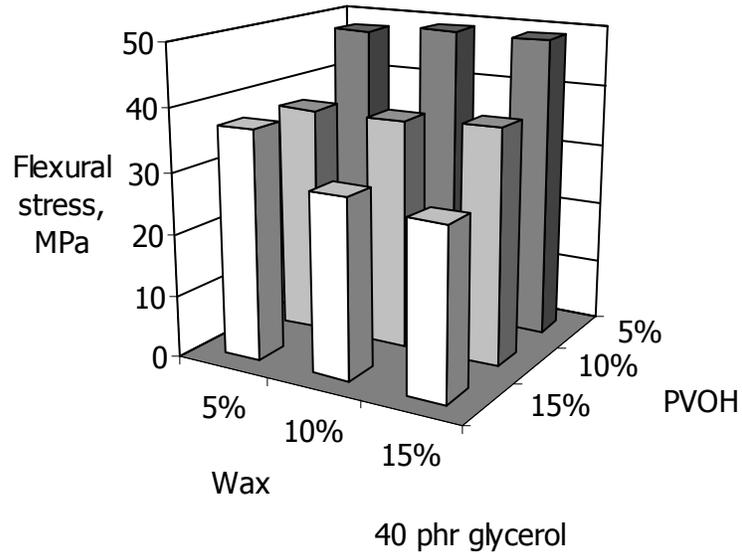


Figure 53: Flexural stress of the urea-wax-PVOH (40 phr glycerol) compound

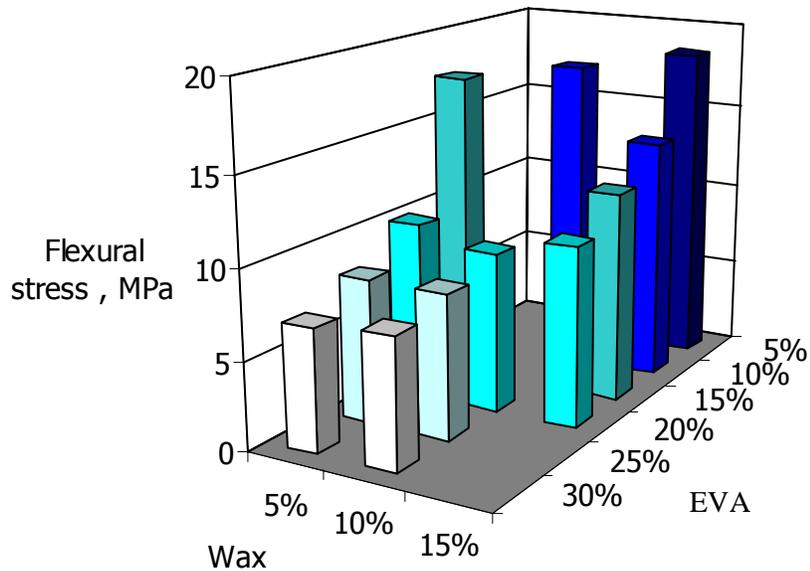


Figure 54: Flexural stress of the urea-EVA-wax compound

At any degree of plasticisation, the flexural stress increases as the polymer content is reduced, as shown in Figures 52 and 53. This is attributed to increases in stiffness as the urea content is increased. Increasing the wax content does not affect the flexural strength to a large extent at any degree of plasticisation. This could be because the wax and PVOH do not form a compatible blend.

As the degree of plasticisation decreases from 80 phr to 40 phr, the intermolecular friction between the PVOH molecules increases, causing the molecules to slip and slide over each other less easily. This increases the rigidity of the PVOH, making it less flexible and increasing the tensile strength and the flexural stress.

The flexural stress data for the EVA moulding compounds are shown in Figure 54. As the EVA content is increased, the flexural stress decreases. This could be explained by the effect of the reduction in the urea content, which is associated with a loss of stiffness. The flexural stress varies little with the wax content.

The PVOH moulding compounds had superior flexural stress compared with the EVA moulding compounds because of strong hydrogen bonding between the urea and the hydroxyl group of the PVOH. In contrast, in the case of the EVA moulding compounds there is a weak bonding interaction between the acetate group (hydrophobic) of the EVA/wax blend and the urea.

The flexural stress of the industrial cooked urea moulding compound (benchmark) was weaker than that of the PVOH moulding compound prepared with a two-roll mill. This could be due to the degradation of the urea as it is cooked above its degradation temperature of 132°C.

Flexural strain

Flexural strain provides a measure of the flexibility of a material. Higher strain-at-break indicates superior flexibility. Excessive flexibility can affect the dimensional stability of moulding patterns during the assembly process in investment casting. Two-way ANOVA was used to analyse the flexural strain results for the urea-based moulding compounds. The results obtained are shown in Tables 22 to 24 below. The experimental data and the predicted data (linear regressed data) are compared in Figures 55 to 57. The regression equations are also given below.

Table 22: Two-way ANOVA for flexural strain of the urea-PVOH-wax compound containing 80 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	0,00016	2	0,00008	21	< 0.001
PVOH	0,00536	2	0,00268	723	< 0.001
Wax*PVOH	0,00047	8	0,00012	32	< 0.001
Error	0,00013	30			
<i>Total</i>	<i>0,00612</i>	<i>44</i>			

Table 23: Two-way ANOVA for flexural strain of the urea-PVOH-wax compound containing 40 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	0,00012	2	0,00006	25	< 0.001
PVOH	0,00058	2	0,00029	121,1	< 0.001
Wax*PVOH	0,00015	8	0,00004	15,52	< 0.001
Error	0,00009	30			
<i>Total</i>	<i>0,00094</i>	<i>44</i>			

Table 24: Two-way ANOVA for flexural strain of the urea-EVA-wax compounds

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	0,00148	2	0,00074	1509,6	0
EVA	0,00296	5	0,00059	1211,3	0
Wax*EVA	0,00057	4	0,00014	292.1	0
Error	0,00002	48			
<i>Total</i>	<i>0,00504</i>	<i>59</i>			

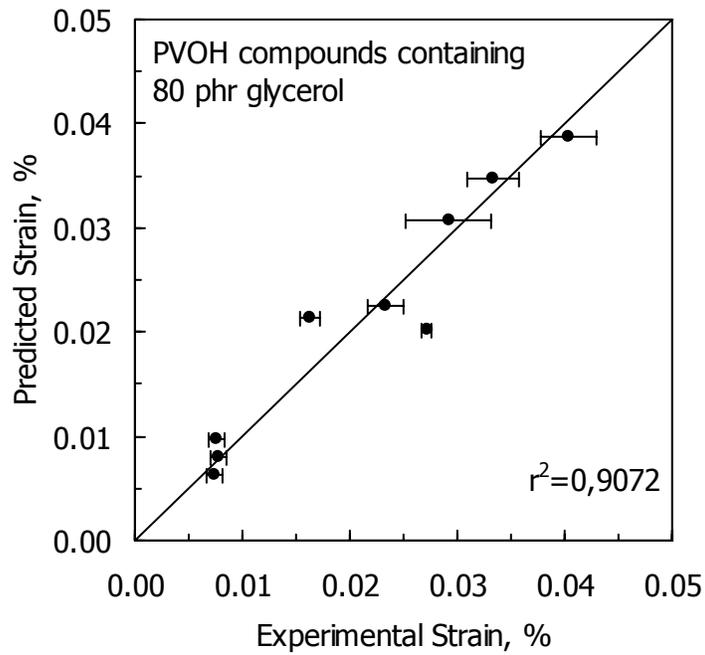


Figure 55: Comparison between predicted and experimental flexural strain for linear model fit of the urea-wax-PVOH (80 phr glycerol) compound data

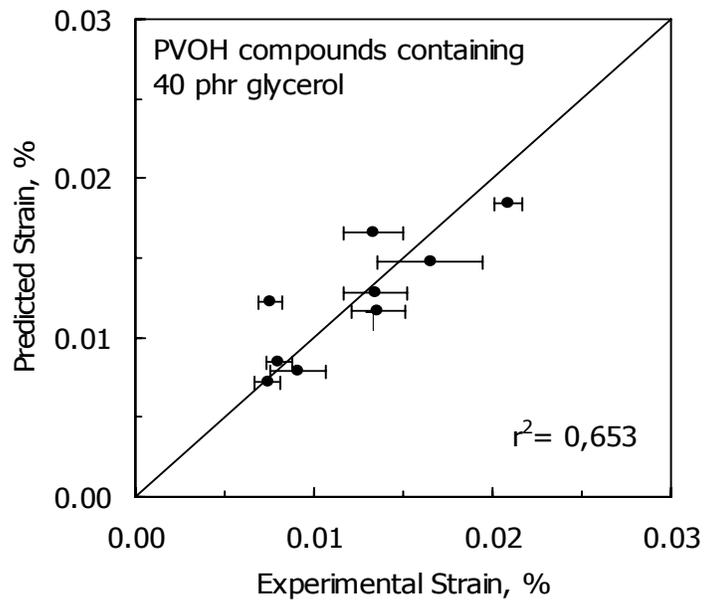


Figure 56: Comparison between predicted and experimental flexural strain for linear model fit of the urea-wax-PVOH (40 phr glycerol) compound data

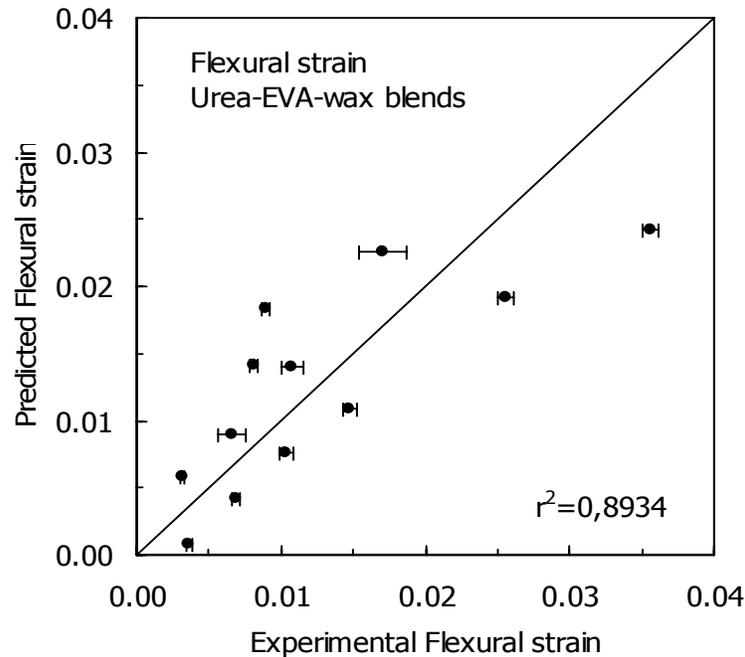


Figure 57: Comparison between predicted and experimental flexural strain for linear model fit of the urea-EVA-wax compound data

Data analysis

The two-way ANOVA results for the PVOH urea-based compounds containing 80 phr and 40 phr glycerol, and for the EVA compounds, are shown in Tables 22 to 24. From the results, the polymer and the waxes, and their interaction, are significant for all the moulding compounds. The linear regression leads to:

PVOH (80 phr glycerol):

$$Y_{Flexural\ strain} = -0,0144 + 0,3815 X_{PVOH} + 0,0908 X_{wax} - 1,1455 X_{wax} X_{PVOH} \quad (r^2 = 0,9027) \quad (37)$$

PVOH (40 phr glycerol):

$$Y_{flexural\ strain} = -0,0003 + 0,1370 X_{PVOH} + 0,0379 X_{wax} - 0,4972 X_{wax} X_{PVOH} \quad (r^2 = 0,653) \quad (38)$$

Urea-EVA-wax:

$$Y_{Flexural\ strain} = -0,0158 + 0,050 X_{EVA} + 0,1317 X_{wax} + 0,341 X_{wax} X_{EVA} \quad (r^2 = 0,893) \quad (39)$$

The results of the data analysed are depicted in Figures 58 to 60 below. In the case of both the EVA and the urea-wax-PVOH (80 phr glycerol) compounds, the model fits well. A poor fit was obtained with the urea-wax-PVOH (40 phr) compound: the linear model only explains 65% of the total variation in the data about the average. Indeed, Figure 56 shows that the response is non-linear.

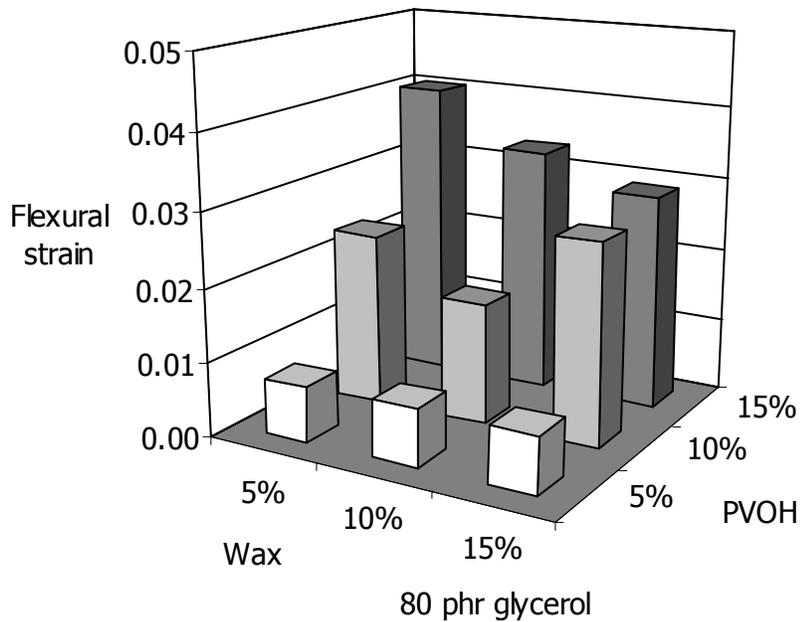


Figure 58: Flexural strain of the urea-wax-PVOH (80 phr glycerol) compound

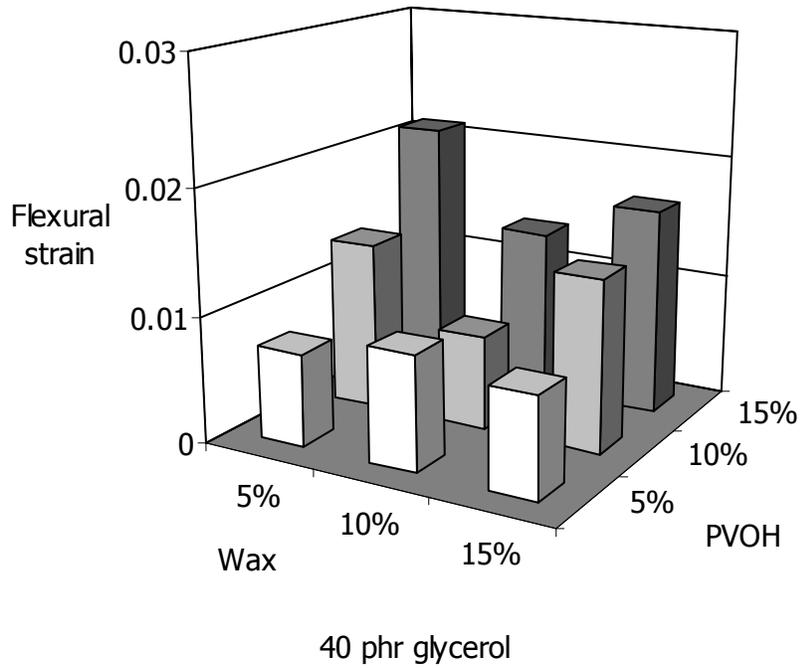


Figure 59: Flexural strain of the urea-wax-PVOH (40 phr glycerol) compound

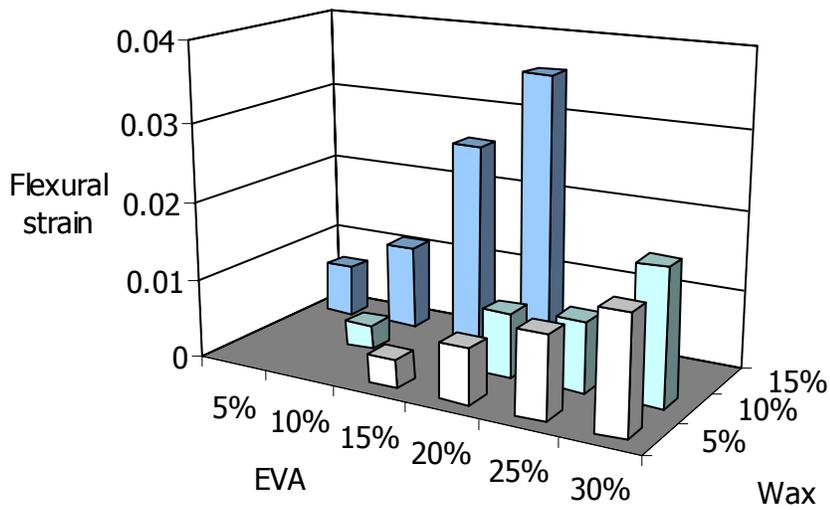


Figure 60: Flexural strain of the urea-EVA-wax compound

The results given in Figures 58 and 59 shows that as the PVOH content is increased, the flexural strain increases as expected for both degrees of plasticisation.

An increase in the wax content slightly affects the flexural strain at any degree of plasticisation. This is because PVOH is highly hydrophilic and wax is hydrophobic and therefore they will resist each other. A decrease in the degree of plasticisation from 80 to 40 phr reduces the flexural strain and vice versa. Based on the definition of plasticisation, the elongation should increase with an increase in the plasticiser concentration. This is because the intermolecular attraction between polymer chains gets weaker as the glycerol content is increased due to the increase in free volume. This improves the flexibility of the PVOH chains, thus increasing the flexural strain. As shown in Figure 60, the flexural strain increases as the EVA content is increased, as expected. An increase in the wax content also increases the flexural strain slightly. This could be explained by the fact that wax forms a compatible blend with EVA.

The flexural strain data show that the PVOH urea-based compounds have greater flexural strain compared with the EVA-urea-based compounds at a given urea content. This could be explained by the type of urea and polymer interactions that occur. The superior flexural strain obtained with the PVOH moulding compounds, compared to the EVA moulding compounds, may be attributed to better compatibility of this polymer with urea through hydrogen bonding interactions and also to the higher molecular mass of this polymer.

The flexural strain of the industrial cooked urea-moulding compound (benchmark) was higher than that of the PVOH and EVA moulding compounds. This could be due to urea's loss of stiffness as it is cooked above its degradation temperature of 132°C.

Fracture energy

The Charpy impact test provides quantitative information on the material behaviour at a very high strain rate (brittle fracture). In contrast, the process of breaking the sample in a three-point bending test provides information on the fracture energy at low strain rates. The moulding compounds studied here showed mostly brittle fracture behaviour. In brittle fracture, the fracture energy equals the work done during the breaking of a sample. It corresponds to the area under a load-versus-deflection curve. The two-way ANOVA results obtained from the

flexural stress experimental data are shown in Tables 25 to 27 below. The experimental data and the predicted data (linear regressed data) are then compared to establish a fit. The regression equations are also given below.

Table 25: Two-way ANOVA for fracture energy of the urea-PVOH-wax compounds containing 80 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	4 858	2	2 429	13,82	< 0,0001
PVOH	44 000	2	22 000	125,2	< 0,0001
Wax*PVOH	2 958	8	739,4	4,21	0,0068
Error	6 328	30	175,8		
<i>Total</i>	<i>58 145</i>	<i>44</i>			

Table 26: Two-way ANOVA for fracture energy of the urea-PVOH-wax compounds containing 40 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	12 544	2	6272	39,6	< 0,0001
PVOH	8 854	2	4 417,8	27,89	< 0,0001
Wax*PVOH	13 606	8	3 401,4	21,47	< 0,0001
<i>Error</i>	<i>5 702</i>	<i>30</i>	<i>158,4</i>		
<i>Total</i>	<i>40 687</i>	<i>44</i>			

Table 27: Two-way ANOVA for Fracture energy urea-EVA-wax compounds

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	17	2	8,677	8,42	0,0007
EVA	1 598	2	319,6	310,27	< 0,0001
Wax*EVA	34	8	8,586	8,34	< 0,0001
Error	49	30	1,030		
<i>Total</i>	<i>1 699</i>	<i>44</i>			

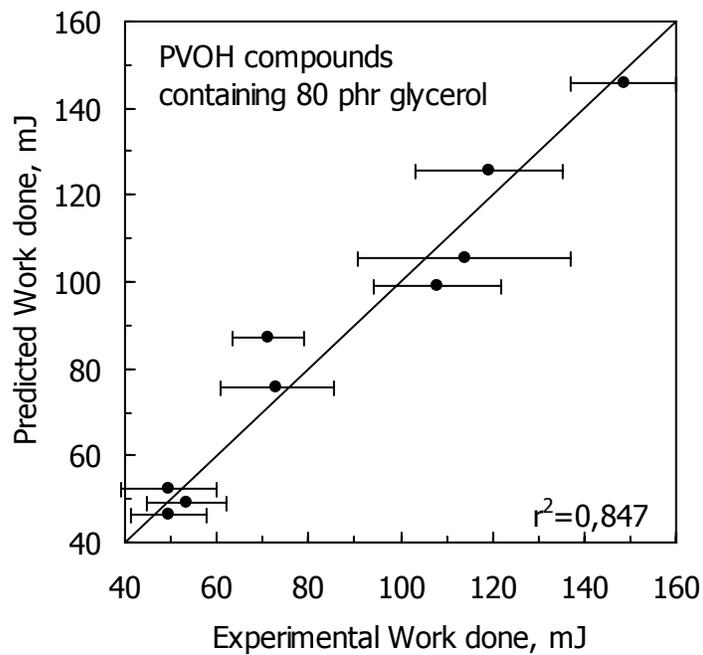


Figure 61: Comparison between predicted and experimental fracture energy for quadratic model fit of the urea-wax-PVOH (80 phr glycerol) compound data

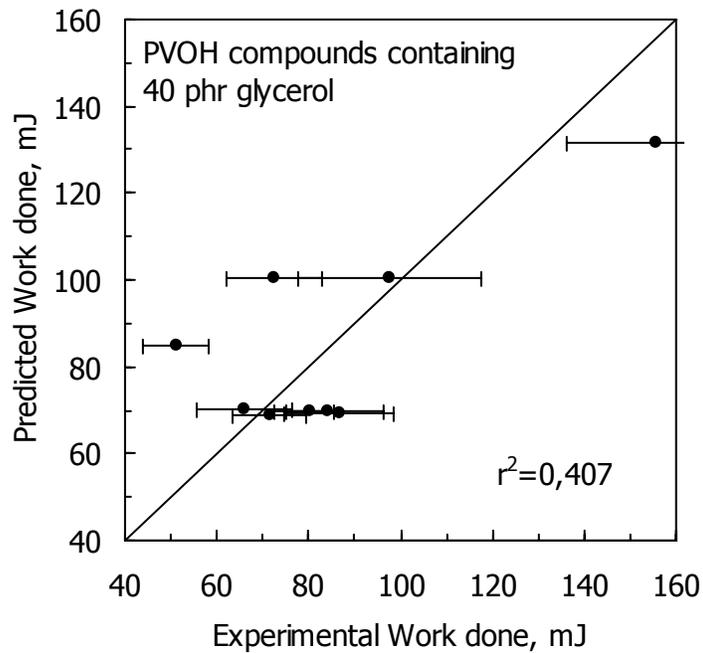


Figure 62: Comparison between predicted and experimental fracture energy for quadratic model fit of UP4 data

Data analysis

The two-way ANOVA results for the PVOH urea-based compounds containing 80 phr and 40 phr glycerol, and for the EVA compounds, are shown in Tables 25 to 27. It is concluded that both the polymer and the wax, and their interaction, are significant in all three cases. Regression yields:

PVOH (80 phr glycerol):

$$Y_{Fracture\ energy} = -0,3 + 1108,8 X_{PVOH} + 113,2 X_{wax} - 3451,0 X_{wax} X_{PVOH} \quad (r^2 = 0,840) \quad (40)$$

PVOH (40 phr glycerol):

$$Y_{fracture\ energy} = 21,20 + 943,7 X_{PVOH} + 330,2 X_{wax} - 6353,2 X_{wax} X_{PVOH} \quad (r^2 = 0,4709) \quad (41)$$

Urea-EVA-wax:

$$Y_{Fracture\ energy} = -6,00 + 71,49 X_{EVA} + 70,32 X_{wax} + 66.536 X_{wax} X_{EVA} \quad (r^2 = 0,8934) \quad (42)$$

In the case of the EVA compound and the urea-wax-PVOH (80 phr glycerol) compound, the model fits with over 85% of the total variation in the data about the average explained. The poor fit seen for the PVOH (40 phr) compound is attributed to the non-linear response evident in Figure 62. The average results of the data analysed are shown in Figures 64 to 66 below.

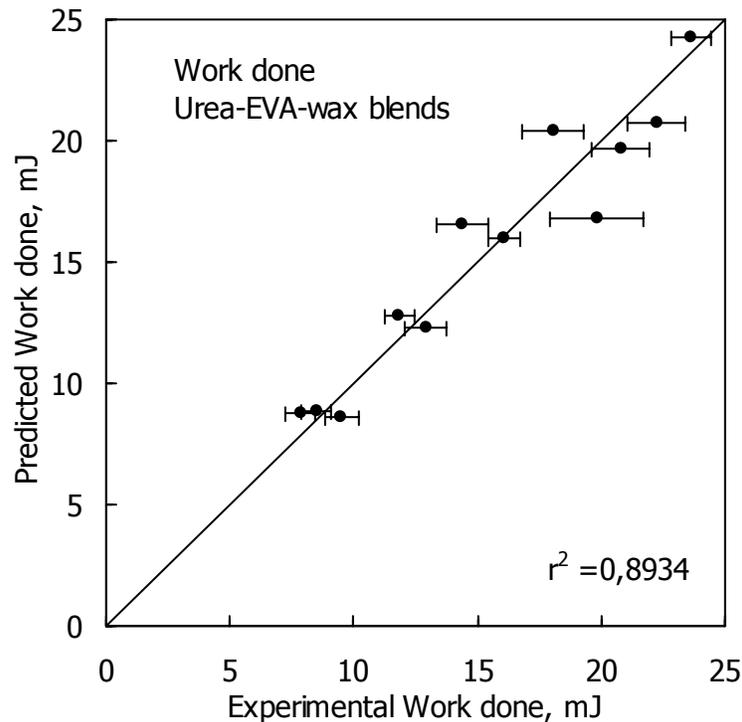


Figure 63: Comparison between predicted and experimental fracture energy for linear model fit of urea-EVA-wax compound data

Figures 64 and 65 confirm that the work done to fracture increases with an increase in the polymer content. This is true irrespective of the degree of plasticisation and implies that the polymer reinforces the urea compound (or increases the ductility which will increase the area under the curve). The microscopic mechanism is not known. However, it may be that the polymer acts as a binder for the urea crystallites i.e. changing from brittle to ductile fracture behaviour.

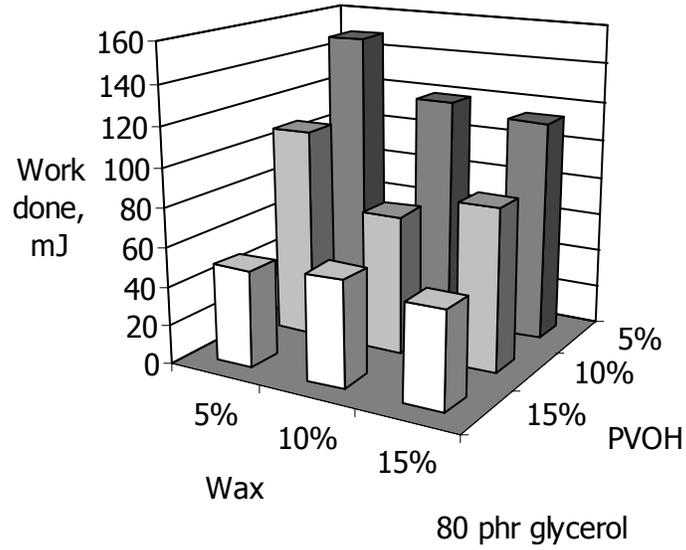


Figure 64: Fracture energy of the urea-wax-PVOH (80 phr glycerol) compounds

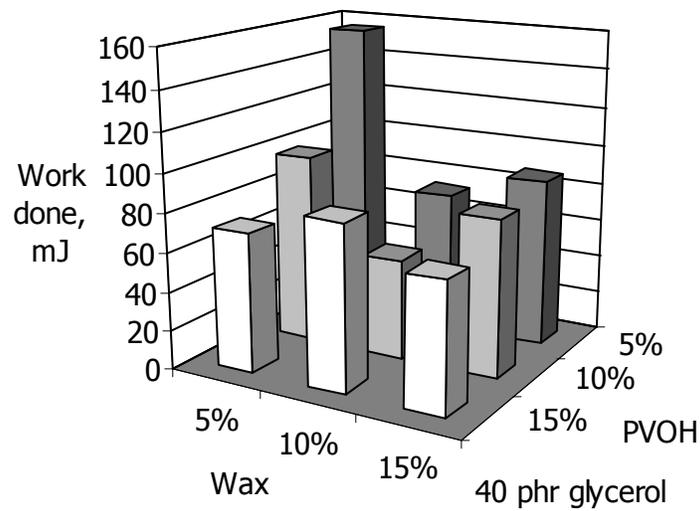


Figure 65: Fracture energy of the urea-wax-PVOH (40 phr glycerol) compounds

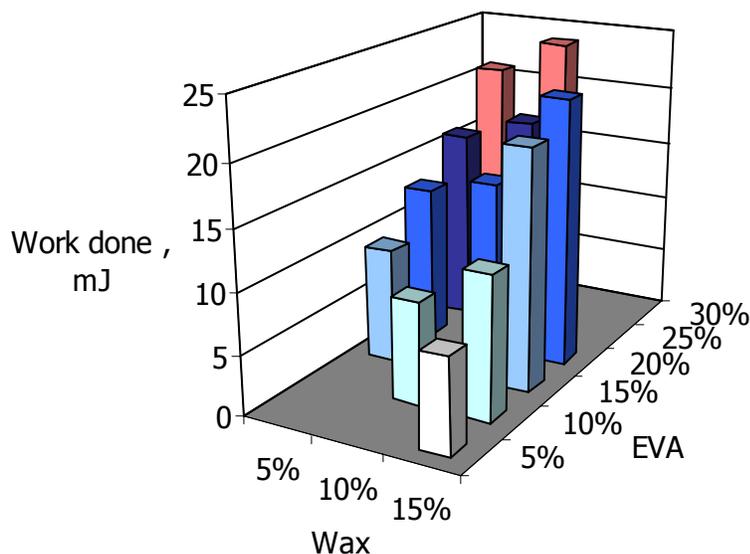


Figure 66: Fracture energy of the urea-EVA-wax compounds

The effect of the wax does depend on the degree of plasticisation. This could be because an increased wax content increases the stiffness and crystallinity slightly, causing a reduction in the deflection point. Since PVOH is highly hydrophilic and wax is hydrophobic, there is little interaction between them. The wax merely acts as an external lubricant to eliminate external friction between the polymer and the metal surface of the processing equipment.

As the degree of plasticisation of the PVOH is increased from 40 to 80 phr, the fracture energy of the urea moulding compound increases. Thus PVOH urea-based compounds containing 80 phr glycerol are tougher. This correlates with the lower glass transition temperature (T_g) for this polymer, i.e. it relates to the theory behind plasticisation. As the amount of glycerol increases, there is a reduction in the intermolecular friction between the polymer molecules, so the molecules can slip and slide over each other more easily, producing a more flexible polymer. This causes the elongation to increase and hence improves the fracture energy (toughness).

The results for the EVA moulding compounds are shown in Figure 66. As the polymer content is increased, a higher value of fracture energy is expected. When the polymer content is increased, flexibility is increased, causing the moulding compound to undergo a greater deflection to break. This is clearly depicted in an increase in the area under the load and deflection point. As the wax content is increased, the fracture energy increases. This shows that the wax acts merely as an internal lubricant, forming a compatible blend with the EVA matrix and thus enhancing the toughness of the EVA urea-based moulding compounds.

The fracture energy shows that the PVOH urea-based moulding compounds are about seven times tougher than the EVA-urea compounds. This depends largely on the urea-polymer interaction. Urea is a hydrophilic organic compound and therefore forms strong hydrogen bonds with the hydroxyl group of plasticised PVOH. The acetate group is highly hydrophobic and therefore interacts weakly with the hydrophilic urea.

The results in Appendix A show that the industrial cooked urea-based compound (benchmark) is not as tough as the PVOH urea-based moulding compounds prepared via the conventional two-roll mill process.

Modulus of elasticity

The modulus of elasticity provides information about the degree of stiffness of a material. The stiffness of a material corresponds to the gradient of the straight line in the load-versus-deflection curve. The modulus of elasticity increases as the slope becomes steeper. The two-way ANOVA results obtained from the flexural stress experimental data are shown in Tables 28 to 30 below. The experimental data and the predicted data (linear regressed data) are then compared in Figures 66 to 68 to establish a fit. The regression equations are also given below.

Table 28: Two-way ANOVA for the modulus of elasticity of the urea-PVOH-wax compounds containing 80 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	1,302	2	0,6508	0,61	0,552
PVOH	244,312	2	61,078	56,88	0
Wax*PVOH	3,665	8	0,4581	0,43	0,8957
Error	32,213	30	1.0738		
<i>Total</i>	<i>281,492</i>	<i>44</i>			

Table 29: Two-way ANOVA for the modulus of elasticity of the urea-PVOH-wax compounds containing 40 phr glycerol

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	13,616	2	6,8082	6,55	0,0044
PVOH	127,850	2	31,9624	30,74	0
Wax*PVOH	18,577	8	2,3221	2,23	0,0531
Error	31,193	30	1,0398		
<i>Total</i>	<i>191,236</i>	<i>44</i>			

Table 30: Two-way ANOVA for the modulus of elasticity of the urea-EVA-wax compounds

Source	Sum-of-squares	Degrees of freedom	Mean square	F	Probability > F
Wax	115,5	2	57,73	164,09	< 0,0001
EVA	822,12	5	164,43	476,4	< 0,0001
EVA*Wax	64,7	4	16,2	46,0	< 0,0001
Error	16,9	48	0,35		
<i>Total</i>	<i>1019,22</i>	<i>59</i>			

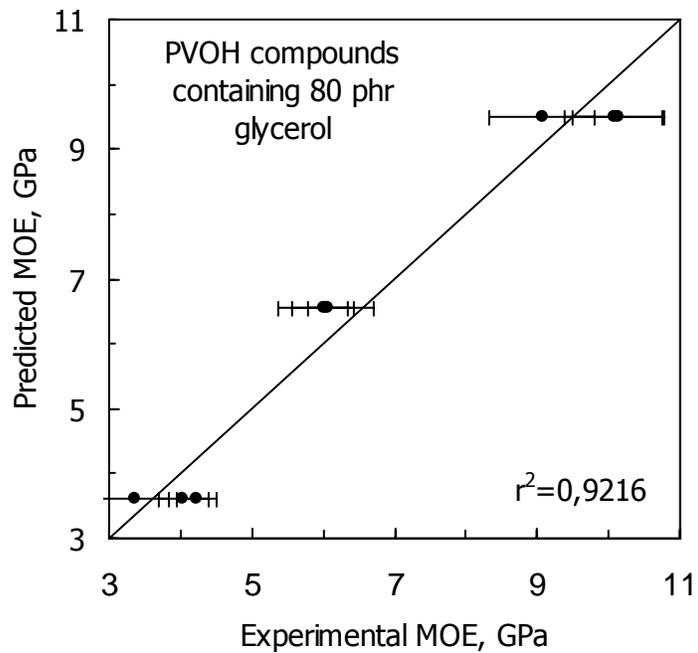


Figure 67: Comparison between the predicted and experimental modulus of elasticity for quadratic model fit of urea-wax-PVOH (80 phr glycerol) compounds

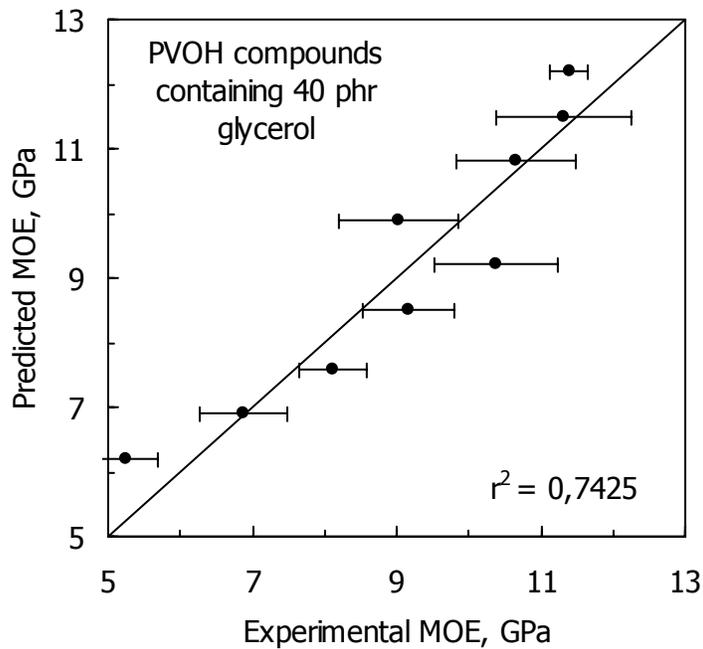


Figure 68: Comparison between predicted and experimental modulus of elasticity for quadratic model fit of urea-wax-PVOH (40 phr glycerol) compounds

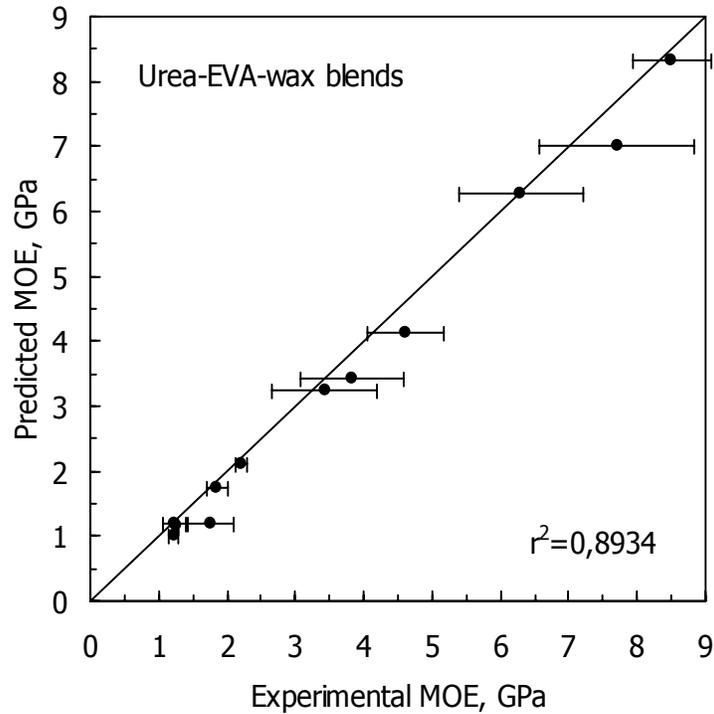


Figure 69: Comparison between predicted and experimental modulus of elasticity for quadratic model fit of urea EVA-wax compounds

Data analysis

It is concluded that both the polymer and the wax, and their interaction, are significant in all three cases. Regression yields:

PVOH (80 phr glycerol):

$$Y_{MOE} = -1,4644 + 54,04 X_{PVOH} + 6,973 X_{wax} - 260,0 X_{wax} X_{PVOH} \quad (r^2 = 0,9216) \quad (43)$$

PVOH (40 phr glycerol):

$$Y_{MOE} = 12,53 + -22,35 X_{PVOH} + 9,75 X_{wax} - 213,80 X_{wax} X_{PVOH} \quad (r^2 = 0,7425) \quad (44)$$

Urea-EVA-wax:

$$Y_{MOE} = -6,00 + 71,49 X_{EVA} + 70,32 X_{wax} + 66,536 X_{wax} X_{EVA} \quad (r^2 = 0,8934) \quad (45)$$

The poor fit seen for the PVOH with 40 phr glycerol is attributed to the non-linear response evident in Figure 68.

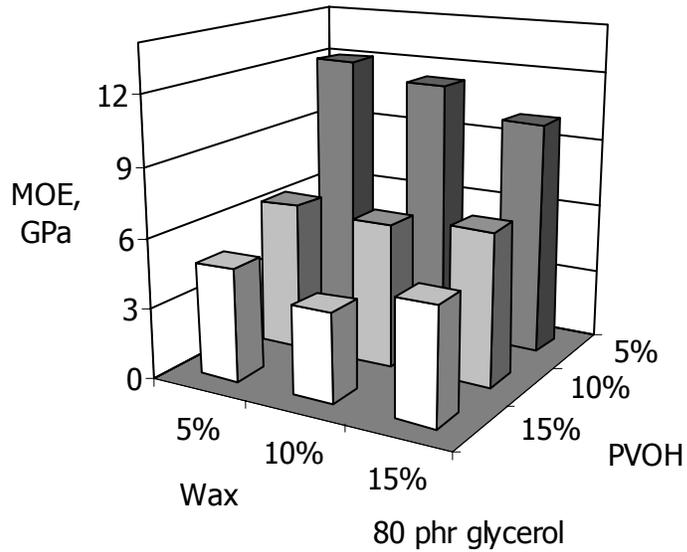


Figure 70: Modulus of elasticity of the urea-wax-PVOH (80 phr glycerol) compounds

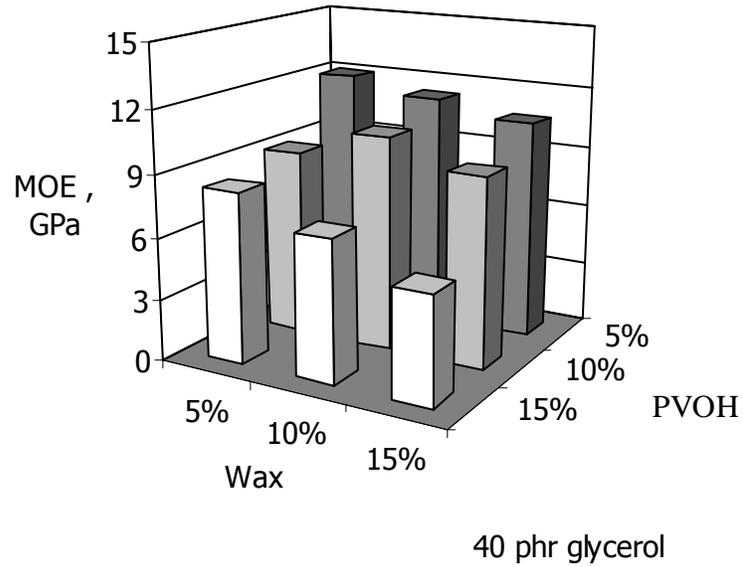


Figure 71: Modulus of elasticity of the urea-wax-PVOH (40 phr glycerol) compounds

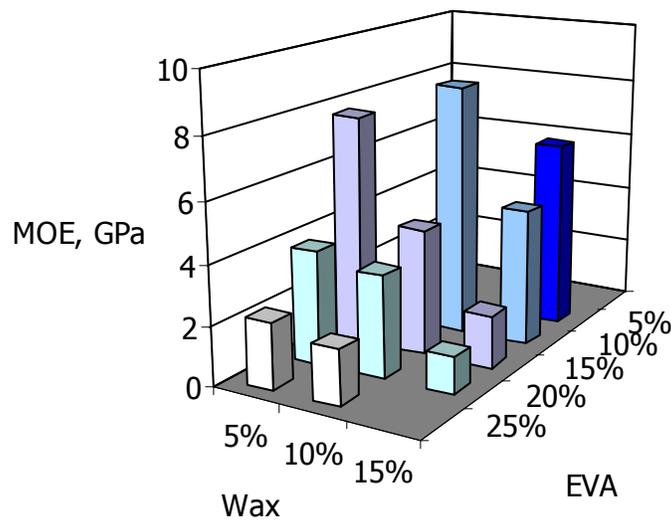


Figure 72: Modulus of elasticity of the urea-EVA-wax compounds

At any degree of plasticisation the modulus of elasticity increases as the polymer content is decreased, as shown in Figures 70 and 71. This is attributed to increases in stiffness as the urea content is increased. Increasing the wax content affects the modulus of elasticity to a small extent at any degree of plasticisation. This could be because the wax and the PVOH do not form any compatible blend. The PVOH is highly hydrophilic and the wax is hydrophobic and therefore they will resist each other.

Increasing the glycerol content in the PVOH from 40 to 80 phr decreased the modulus of elasticity. This is because the tensile strength is reduced and the percentage of elongation is increased.

The modulus of elasticity data for the EVA compounds is shown in Figure 72. As the EVA and wax contents are increased, the modulus of elasticity falls. Firstly, this could be explained by the effect of reducing the urea content, which reduces stiffness. Secondly, wax and EVA form compatible blends, which will contribute to the same effect.

The modulus of elasticity of the PVOH urea-based moulding compounds is approximately double that of the EVA moulding compounds at a given urea content. This could be explained by the type of filler used and by the polymer interactions that take place. PVOH forms strong hydrogen bonds with urea because of the presence of the hydroxyl group, whereas in the EVA moulding compounds there is only a weak interaction between the hydrophobic acetate group and urea.

The PVOH moulding compounds have superior moduli of elasticity compared with the cooked urea-based compound. This could be explained by the fact that the cooking process destroys the structural properties of urea when it is heated above its degradation temperature.

8.4 Dynamic mechanical analysis

Polymers are viscoelastic materials, i.e. they exhibit properties characteristic of viscous liquids and elastic solids. The mechanical properties of polymers depend on temperature. They are also time-dependent. This temperature-time-dependent relaxation behaviour can be studied using the stress-strain relationship generated by dynamic mechanical analysis (DMA). The main

variables measured in DMA are the storage modulus (E'), which represents the elastic modulus; the loss modulus (E'') representing the viscous component, and the damping factor ($\tan(\delta)$), defined as the ratio of E''/E' . The experimentally determined dynamic mechanical behaviours of the urea-based moulding compounds are depicted in Figures 73 to 80.

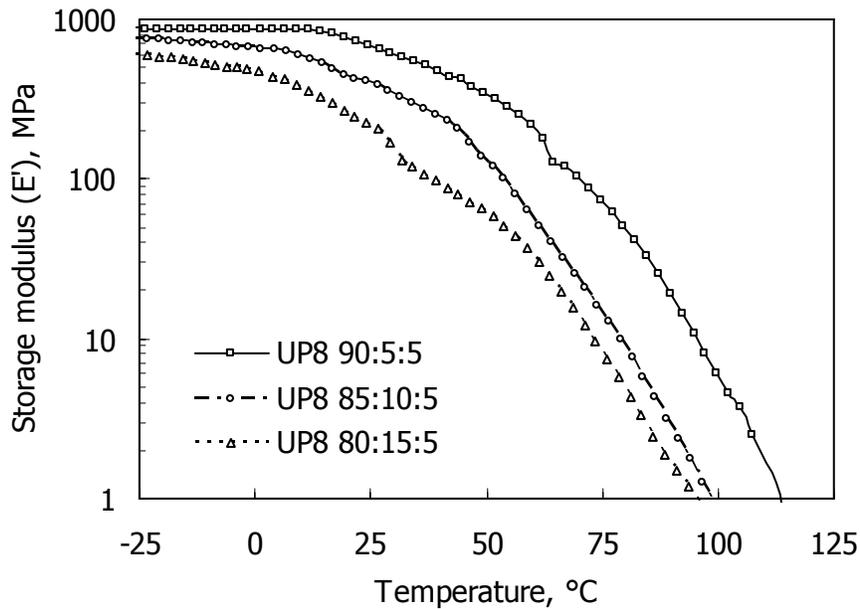


Figure 73: Effect of increasing the polymer content on the storage modulus versus the temperature of the urea-PVOH moulding compounds

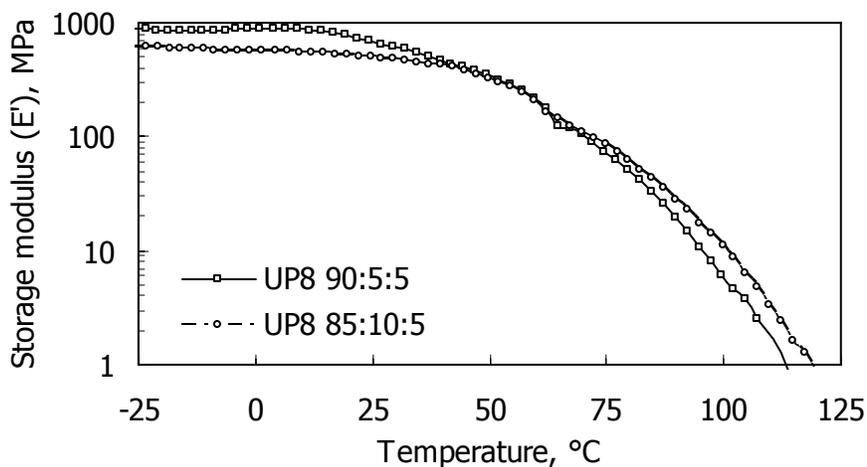


Figure 74: Effect of increasing the wax content on the storage modulus versus the temperature of the urea-PVOH moulding compounds

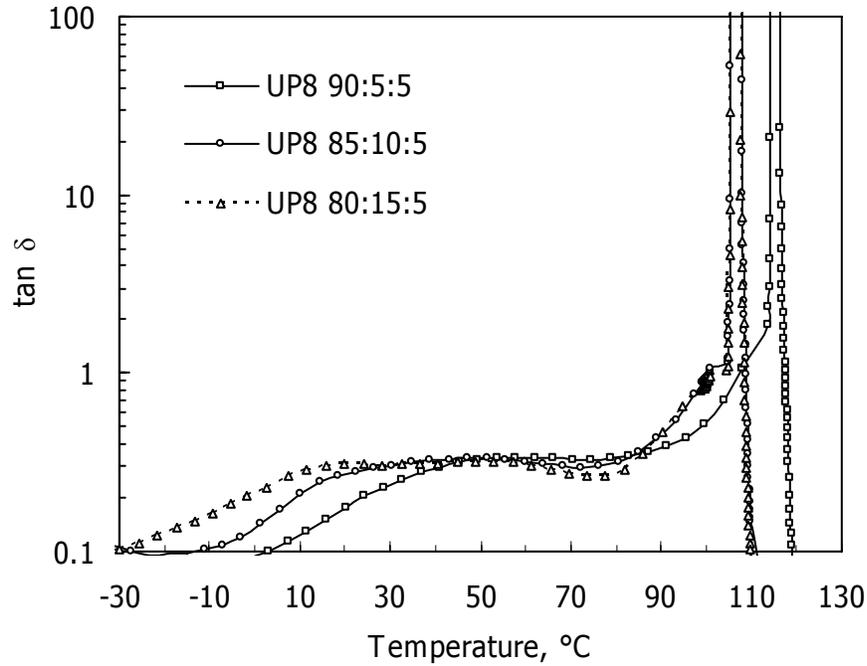


Figure 75: Effect of increasing the polymer content on the damping factor versus the temperature of the urea-PVOH moulding compounds

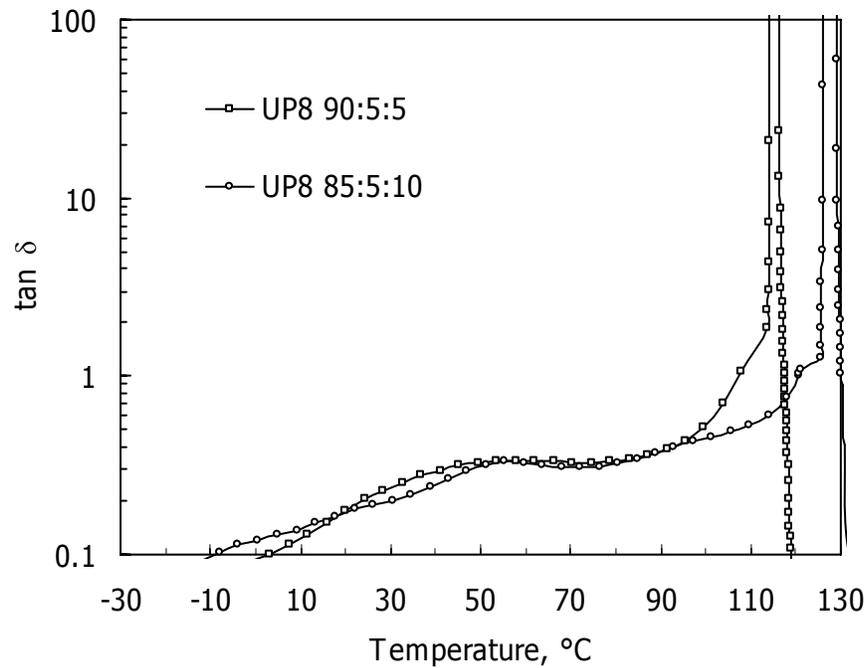


Figure 76: Effect of increasing the wax content on the damping factor versus the temperature of the urea-PVOH moulding compounds

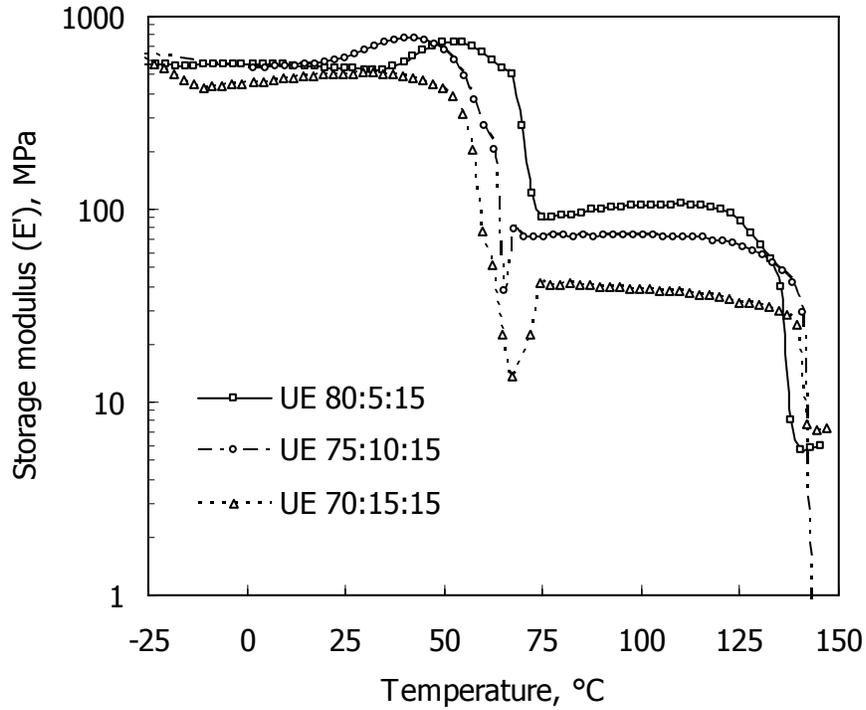


Figure 77: Effect of increasing the polymer content on the storage modulus versus the temperature of the urea-EVA moulding compounds

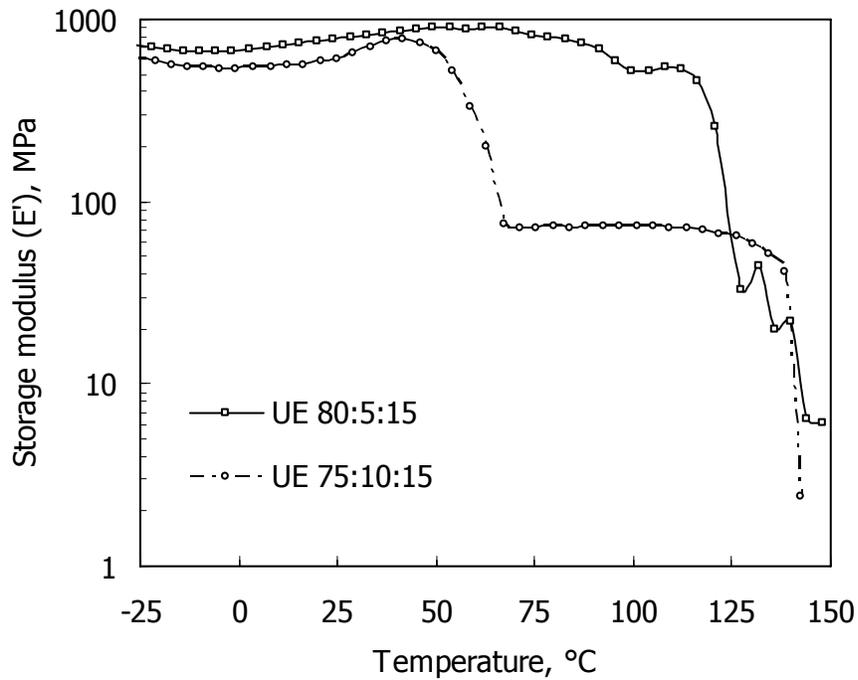


Figure 78: Effect of increasing the wax content on the storage modulus versus the temperature of the urea-EVA moulding compounds

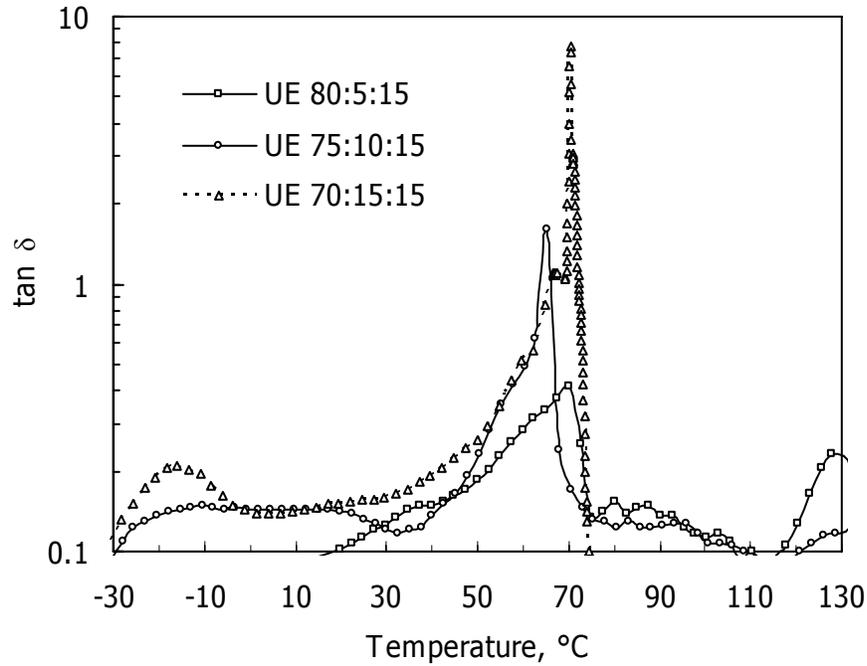


Figure 79: Effect of increasing the polymer content on the damping factor versus the temperature of the urea-EVA moulding compounds

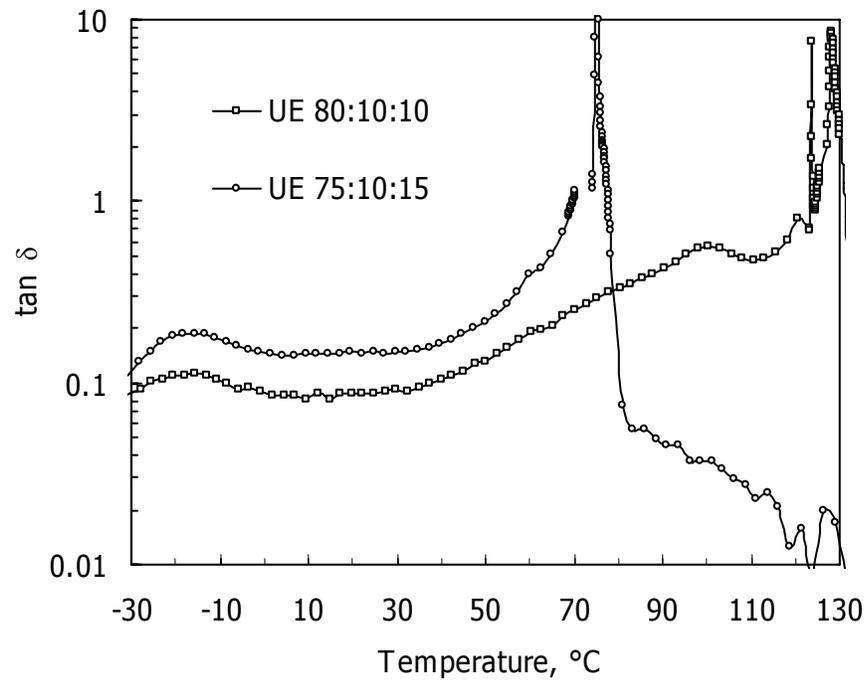


Figure 80: Effect of increasing the wax content on the damping factor versus the temperature of the urea-EVA moulding compounds

Increasing the temperature, the polymer (PVOH) content or the wax content results in a reduction in the storage modulus (Figures 73 and 74). This implies that solid urea is stiffer than plasticised PVOH or wax. The loss modulus (E'') shows the energy lost as heat is evolved.

The damping factor ($\tan \delta$) is defined as:

$$\tan \delta = \frac{E''}{E'} \quad (46)$$

Where E'' is the loss modulus and E' is the elastic modulus

A higher value of $\tan (\delta)$ implies that the material has liquid-like rather than elastic solid properties. Figures 75 to 76 show strong $\tan (\delta)$ peaks between 100 and 110°C. The peaks probably indicate that the amorphous PVOH-glycerol-urea phase of the material has become highly fluid.

The storage modulus versus temperature for the urea-EVA moulding compounds is shown in Figures 77 and 78. The storage modulus decreased systematically with an increase in temperature, wax content or EVA content. A step-wise drop is noted at temperatures above 50°C and is attributed to the melting of the semi-crystalline wax-EVA phase of the material. The steep drop in the storage modulus above 100 °C is due to the melting of the urea phase.

Figures 79 and 80 show a weak $\tan (\delta)$ peak between -10°C and 30°C, and strong $\tan (\delta)$ peaks between 55°C and 65°C and between 125°C and 130°C. The first and second peaks correspond to the glass transition temperature (T_g) and the melting of the EVA/wax phase, while the highest temperature peak indicates melting of the urea phase. The peaks of the EVA/wax blend increase with an increase in the EVA or wax content. This confirms that the EVA/wax blend is a separate phase in the compound. The DMA results are consistent with the DSC observations with respect to the phase-separated nature of the compounds.

To conclude, the DMA results are consistent with the behaviour of phase-separated compounds in which the urea crystals act as reinforcing filler and the polymers and wax act as binder. Thus the stiffness relates directly to the urea content. That is why the PVOH-based compounds are stiffer than the EVA-based moulding compounds. The variation in the DMA storage modulus with

composition is consistent with the corresponding results obtained for the modulus of elasticity in the three-point bending tests.

8.5 Thermal expansion properties

Investment casting pattern materials such as wax expand and contract with changes in temperature. The extent of thermal expansion of the material is crucial as it determines the pressure that will be generated in the green ceramic shell when the moulding compound is removed by a heat treatment. Shrinkage occurs which also affects the dimensional stability of a wax pattern. Fillers are added to wax mainly to reduce the thermal expansion coefficient and reduce expansion during heating.

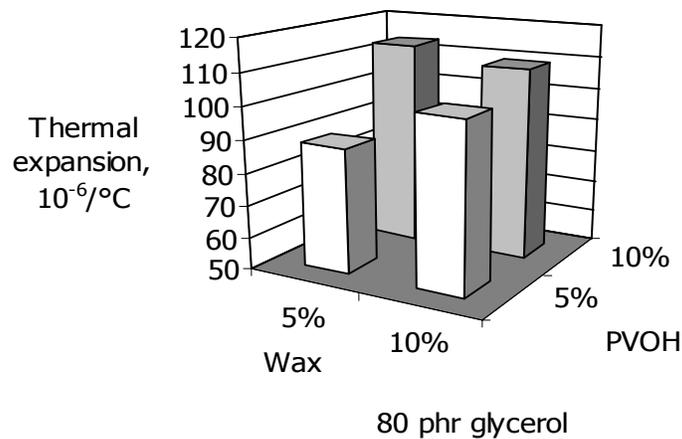


Figure 81: Thermal expansion coefficients measured at various temperatures for the PVOH (80 phr glycerol) compounds measured at 30°C - 40°C

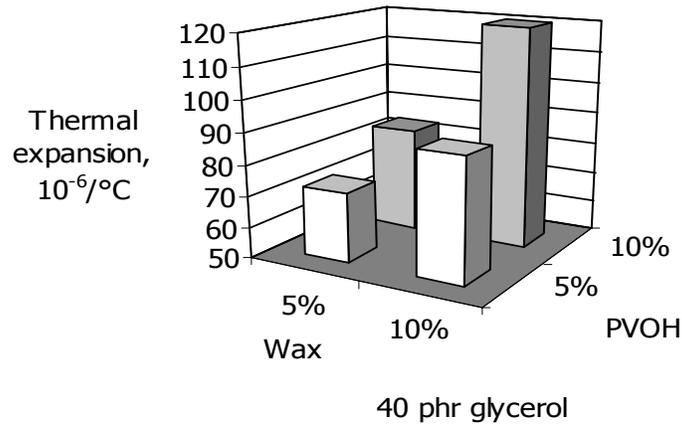


Figure 82: Thermal expansion coefficients measured in the temperature range 30 - 40 °C for the PVOH (40 phr glycerol) compounds

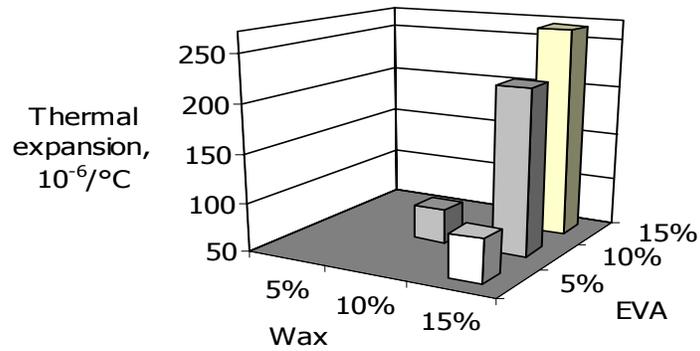


Figure 83: Thermal expansion coefficients measured in the temperature range 30 - 40 °C for the EVA moulding compounds

Figures 81, 82 and 83 show that as the polymer or the wax contents are increased, the linear thermal expansion coefficient increases. This is because the polymeric phases have a much higher thermal expansion than urea.

Similar results from the effect of increasing the wax or polymer contents were shown by the EVA moulding compounds this is shown in Figure 83. However, the PVOH moulding compounds have superior thermal expansion coefficients because there are more highly filled with urea than the EVA moulding compound.

8.6 Melt flow index

The melt flow index (MFI) quantifies the ease of flow of a polymer. It is defined as the weight of polymer in grams flowing in 10 minutes (g/10min) through a capillary of a specific diameter. Polymer systems with high MFIs are easier to process during the extrusion, injection moulding and de-waxing processes. It proved impossible to obtain reliable MFI data with the urea-wax-PVOH compounds containing less than 10% polymer or wax. This is attributed to gross phase separation taking place during the heating stage and to the urea degrading when heated at 110°C for 5 to 10 minutes. Relevant data could only be obtained at levels of 10% polymer and wax or more. The urea-wax-EVA moulding compounds did not show this behaviour.

Figure 84 shows that the MFI increases with an increase in the polymer content, as expected. The blend MFI decreases because urea acts as filler, increasing the viscosity and reducing the ease of flow.

As the wax content is increased, the MFI increases when the PVOH content is 10%. However, at 15% PVOH, additional wax showed little effect: the wax may be acting as an external lubricant but the glycerol plasticiser could have a similar action.

Figure 85 shows that a decrease in the degree of plasticisation from 80 to 40 phr reduces the MFI. Adding more plasticiser would increase the MFI of the base polymer but could also increase the MFI via an external lubrication effect.

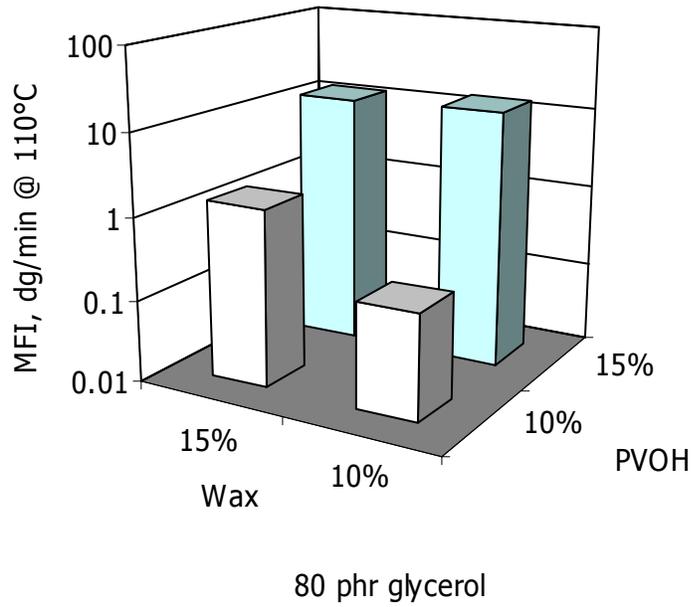


Figure 84: MFI of the urea-wax-PVOH (80 phr glycerol) compounds

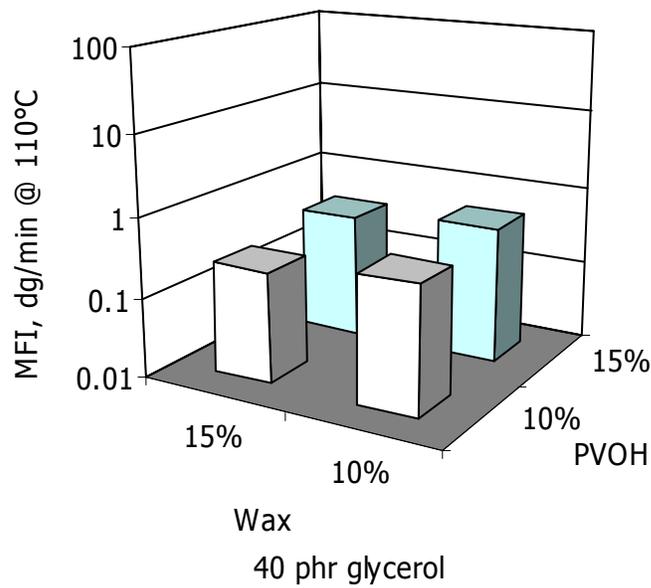


Figure 85: MFI of the urea-wax-PVOH (40 phr glycerol) compounds

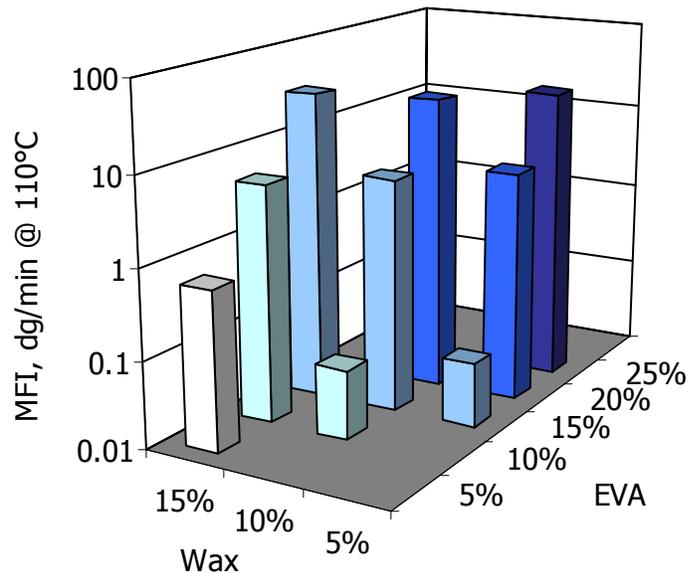


Figure 86: MFI of the urea-EVA-wax moulding compounds

Figure 86 shows that an increase the wax or EVA contents causes the MFI to increase. This is because the wax acts as an internal lubricant and also because it forms compatible blends with EVA.

The MFI of the urea-EVA blend decreases as the urea content is increased. This is because, at the temperatures and pressures at which the measurements were taken, urea will be a solid particulate phase, i.e. it will act as filler. Fillers increase the viscosity of liquids. This explains the difficulties encountered when it was attempted to inject EVA moulding compounds containing 80% or more of urea.

The cooked urea-based moulding compound had better flow properties than any of the PVOH or EVA moulding compounds prepared in this study. Its MFI was 45.58 dg/min at 110°C as indicated in Appendix E.

8.7 Scanning electron microscopy

A rough surface on a pattern will give a rough surface on the ceramic mould which, in turn, will result in a rough-surfaced finished metal part. This metal part will then require machining following the investment casting stage. This adds unnecessarily to the manufacturing cost and must therefore be avoided. This study used scanning electron microscopy (SEM) to investigate (superficially) the surface of injection-moulded samples of the moulding compounds. The effect of composition on the surface texture was studied using a qualitative assessment.

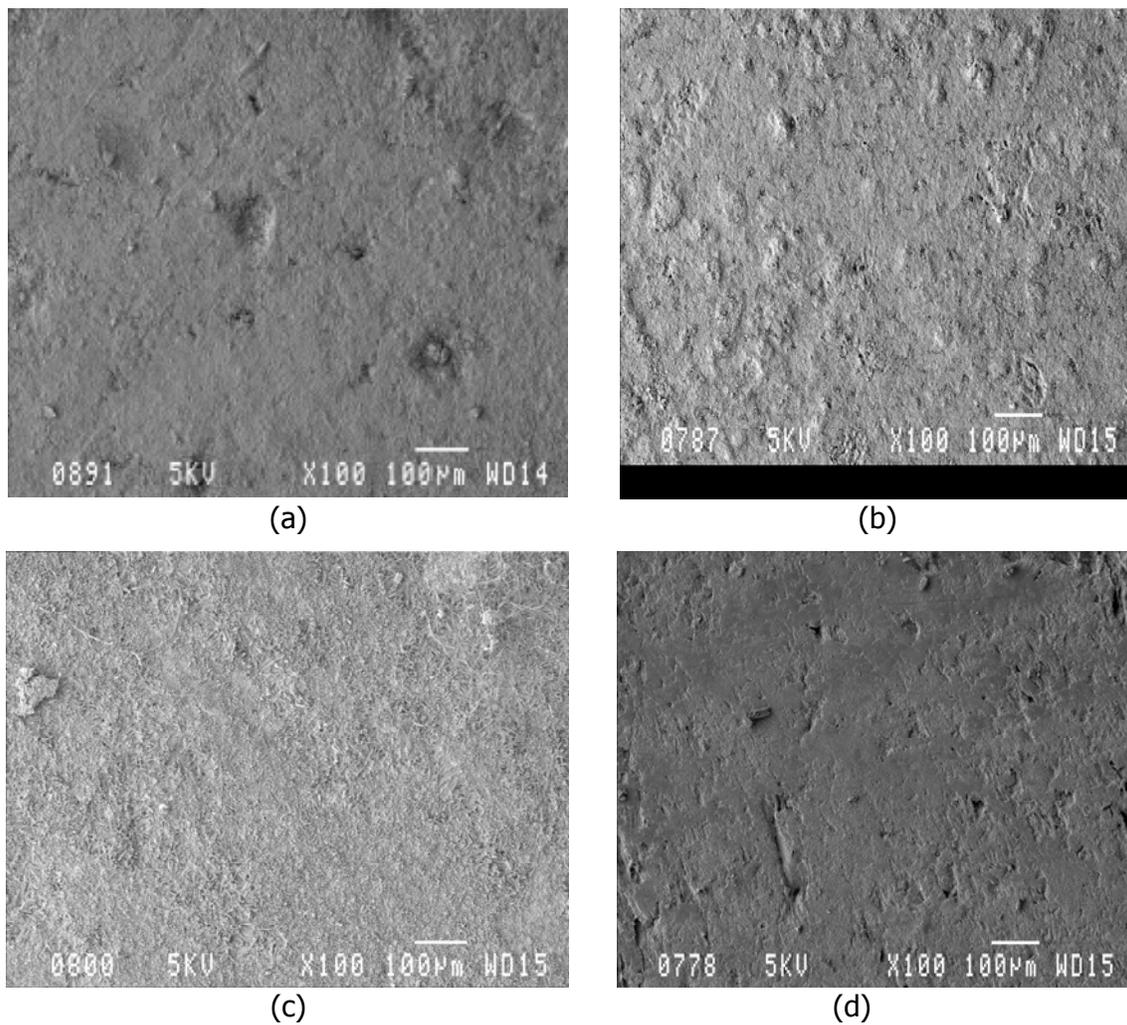


Figure 87: SEM photographs of the surfaces of specimens of the PVOH urea-based moulding compounds: (a) UP8 90:5:5, (b) UP8 85:5:10, (c) UP8 80:5:15 and (d) cooked urea (benchmark)

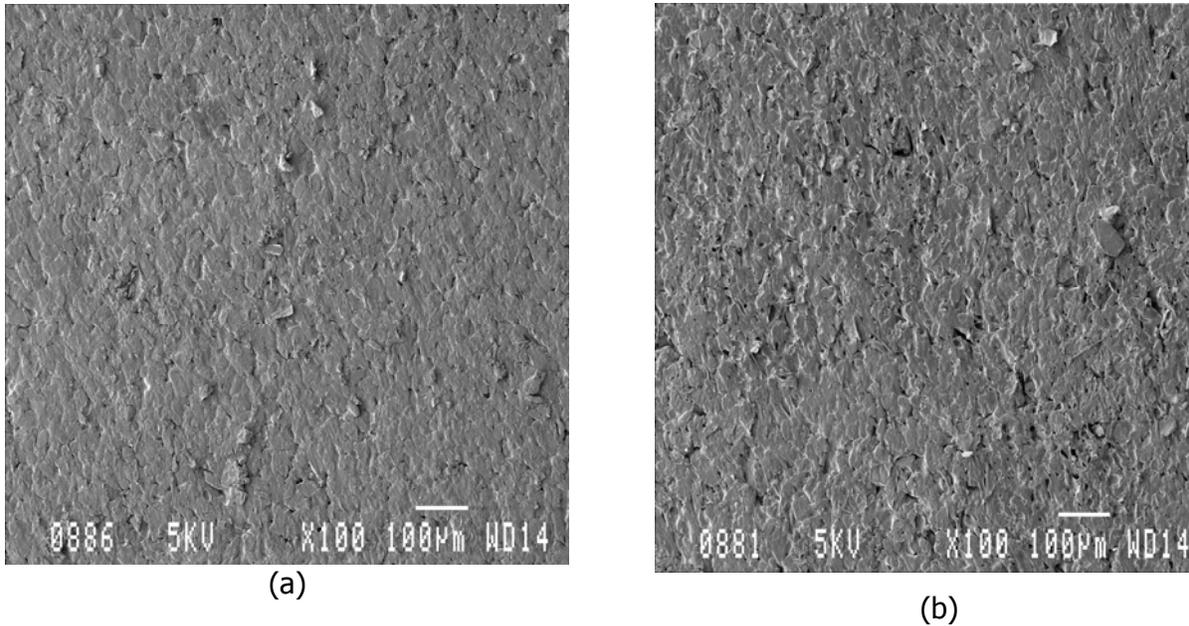


Figure 88: SEM photographs of the surfaces of specimens of the EVA-urea-based moulding compounds: (a) UE 70:20:10 and (b) UE 80:10:10

Figures 87 and 88 show the surface appearance of injection-moulded specimens used in the tensile strength tests. All the photos show surface inhomogeneities. Increasing the wax content appears to cause an increase in the surface roughness (Figure 87) of the PVOH urea-based compounds. The cooked urea-based moulding compound (benchmark) and the two-roll milled PVOH urea-based moulding compound have similar surface appearances.

Figure 8 shows that a slightly smoother surface is obtained when the EVA content is increased. It is evident that the PVOH moulding compound has a smoother surface texture than the EVA compound. The SEM photos also suggest that the reason might be poorer adhesion between the phases in the EVA-based compound. This is because EVA which is hydrophobic has weak interaction with the urea which is hydrophilic.

8.8 Density

The density of the compound is an important aspect in relation to the mixing of pattern during wax injection. Tables 31 and 332 list the densities of the current formulations. The densities of the raw materials are given in Table 31. The density of cooked urea moulding compound was 1,120 g/cm³.

Table 31: Theoretical and measured densities of the EVA-urea-based compounds

	Measured density (g/cm ³)	Theoretical density (g/cm ³)
UE 80:15:5	1,137	1,210
UE 80:10:10	1,168	1,192
UE 80:5:15	1,139	1,174
UE 75:10:15	1,145	1,151
UE 70:15:15	1,121	1,136

Table 32: Theoretical and measured densities of the PVOH urea-based compounds

	Measured density (g/cm ³)	Theoretical density (g/cm ³)
UP8 90:5:5	1,280	1,274
UP8 85:10:5	1,256	1,271
UP8 80:15:5	1,259	1,268
UP8 80:10:10	1,2253	1,228
UP8 80:5:15	1,2332	1,192

Table 33: Density of the raw materials

	Measured density (g/cm ³)
Urea	1,32
Glycerol	1,26
PVOH	0,64
EVA	0,95
Paraffin wax	0,75

As shown in Tables 29 and 30, the density increased as the urea contents increased but were slightly lower than the theoretical density. The measured values were invariably lower, suggesting a degree of porosity in the samples.

CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

Traditional wax-based investment casting involves the following key steps:

- Making of a disposable pattern by injecting wax into a metal mould
- Building a ceramic shell mould by repeatedly dip-coating the pattern in ceramic slurries
- Dewaxing the green ceramic shell
- Firing it to prepare the final ceramic mould
- Casting the molten metal into the shell mould, and
- Removing the shell by mechanical or chemical means to leave a near-net shape metal part.

Urea is a low-cost material and its widespread availability and low toxicity make it an attractive material for investment casting moulding compounds. Indeed, urea is used for this purpose (as a wax replacement) with polyvinyl alcohol (PVOH) used as binder. However, owing to their higher viscosities, the urea-based moulding compounds are injection-moulded just like conventional plastics. Nevertheless, the conventional cooking process requires the preparation of a water-ethanol solution and the subsequent evaporation of the solvents. This study found that it is possible to prepare such urea-based moulding compounds using a conventional polymer compounding procedure. Two systems were investigated:

- With PVOH as binder, it was necessary to plasticise the polymer. It was found that glycerol was a suitable plasticiser which lowered the processing temperature sufficiently to allow the incorporation of urea without it degrading.
- A low-melting EVA also provided a suitable binder for the urea but continuously processable formulations had lower urea contents.

The conventional cooked urea-based compound was used as benchmark composition. This study investigated the effect of the composition on the properties of the two types of compound investigated. Two-way ANOVA was used as a statistical tool to determine which variable had a significant effect. The properties of the two preferred compositions developed and tested in this study are presented in Table 34.

Samples were compounded on a two-roll mill and also on a co-rotating twin-screw compounder. It was possible to injection mould PVOH urea-based moulding compounds with a urea content of up to 90% which had been compounded using a two-roll mill. Using the conventional extrusion process, it was also possible to compound and injection mould EVA urea-based moulding compounds containing up to 70% urea content.

The thermal properties of the compounds are relevant to the pattern's injection-moulding step. Urea degrades just above its melting point of 132°C and this sets an upper limit to the processing temperature. Important factors are the lowest temperature at which the material becomes flowable, and thus mouldable, and the rate of crystallisation. The latter affects the injection-moulding cycle time. The sub-cooling required before crystallisation sets in provides an indication of the material's propensity to crystallise rapidly.

The EVA urea-based moulding compounds showed two endothermic melting peaks and multiple exothermic crystallisation peaks in the DSC curves. The peak at ca. 55 -66°C corresponds to the melting of the wax/EVA blend, while the large peak at 130-132°C corresponds to the melting of the urea. The DSC heating curve of the PVOH urea-based moulding compounds showed two endothermic peaks. The small peak corresponds to the melting of the wax, while the large peak corresponds to the melting of the urea/PVOH blend. The cooked urea-based moulding compound showed one endothermic peak and it had the lowest melting point. Both the wax and polymer contents affected the rate of crystallisation, as evidenced by the high on-set temperature in the DSC cooling curves. However, the composition dependence was found to be highly non-linear.

The moulded patterns should have reasonable mechanical properties, allowing them to survive the wear and tear of the ordinary handling commonly encountered in a manufacturing plant. This study used three-point bending as the primary indicator of mechanical properties, i.e. strength (flexural stress), stiffness (flexural modulus) and deformation limit (flexural strain). In addition, unnotched Charpy impact strength was used as a measure of toughness. Table 32 shows that the PVOH urea-based moulding compound had better mechanical properties than the industrial benchmark. The mechanical properties of the EVA urea-based compound were

generally lower. This is not surprising as the EVA was of a grade with a low molecular mass and it was not expected to interact as strongly with urea (due to hydrogen bonding) as the PVOH.

The effect of the wax and polymer content on the mechanical properties was as follows:

- Increasing polymer content produced weaker but tougher moulding compounds.
- Increasing wax content improved the strength and stiffness but gave compounds that were less tough.
- Two-way ANOVA indicated significant polymer-wax interactions.

The urea content determined the stiffness (elastic modulus) of the compounds. PVOH mouldings had superior stiffness compared with the EVA and cooked urea-based mouldings. The DMA results confirmed the result obtained from the modulus of elasticity in the three-point bending test.

The unnotched Charpy impact test was used to quantify the impact strength in order to determine the toughness of the moulding compounds. The impact strength increased with an increase in polymer content and reduced with an increase in wax content.

The coated patterns are heated to “de-wax” the green shells. In this process step it is necessary that the thermal expansion of the pattern material should be sufficiently low for the green shells not to crack. The linear thermal expansion coefficient generally decreased as the urea content was increased. The measured values were comparable to those of the benchmark and ranged from 100 to 156 x 10⁻⁶ °C.

Viscosity is an important parameter in the “de-waxing” process of the green shells. Once molten, the moulding compound should have a low viscosity (high fluidity) to allow it to flow out of the shells easily. The melt flow index (MFI) of a compound is proportional to the inverse of the viscosity and thus provides a measure of the fluidity. The MFI measured at 110°C was taken as a measure of the fluidity of the compound. The benchmark MFI was higher than that of the two compounds proposed as alternatives. The cooked urea-based moulding compound had the lowest viscosity at 110°C, as indicated by its MFI. This suggests that it would be more difficult to remove the PVOH and EVA moulding compounds from the ceramic shell.

Table 34: Properties of the cooked urea moulding compound (benchmark) compared with those of the best PVOH and EVA moulding compounds

Property	Units	Cooked urea (benchmark)	UP4 90:5:5	UE 70:20:10
Mechanical properties				
Three-point bending test				
Flexural stress	MPa	37,0	47,7	9,15
Flexural strain	%	0,92	0,74	0,81
Modulus of elasticity	GPa	8,5	11,4	3,43
Fracture energy	J	67,7	71,44	14,4
Charpy impact strength	kJ/m ²	0,56	0,84	1,95
Thermal properties				
Ash content (residue at 800 °C)	Mass, %	1,31	0,37	0,0
Temperature to 97% mass loss	°C	472	498	365
Flow properties				
MFI	dg/min@ 110°C	44,5	6,45	24,4
Thermo-mechanical properties				
Linear thermal expansion coefficient	10 ⁻⁶ °C	121	100	156
Vicat softening temperature	°C	57,2	74,5	76,5
Dynamic mechanical properties				
Storage modulus @ 25 °C	10 ⁸ Pa	5,66	6,85	4,89

Once most of the moulding compound has been removed from the shells, the rest should decompose to leave very little residue. This property was characterised by the ash content as measured from the residue remaining at 800°C in the thermogravimetric analysis (TGA). The TGA results confirmed that both the PVOH and EVA urea-based moulding compounds decomposed readily and left less than 1% ash.

Good-quality metal parts should have an acceptable surface finish. This implies that the patterns should have an acceptable surface texture. Scanning electron microscopy (SEM) was used to get

a qualitative idea of the surface and it was found that injection-moulded samples of the cooked and PVOH urea-based moulding compounds gave similar surface finishes. The apparent surface roughness appeared to increase with wax content. The EVA urea-based moulding compound had an irregular surface texture. This could be because of weak interaction of hydrophobic EVA with hydrophilic urea.

Polyvinyl alcohol is fully biodegradable. It also tolerates higher urea contents than the EVA binder. Use of the PVOH urea-based moulding compound is therefore preferable based on its cost-effectiveness and environmental friendliness. However, conventional extrusion-compounding processes can be used to manufacture of the EVA-urea compound. This process has the added advantage that the need for the energy-intensive evaporation of the solvents necessary in the conventional cooking process can be avoided.

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APPENDICES

Appendix A: Physical and chemical properties of material used

The following tables show the chemical and physical properties and the suppliers of the materials used.

Table A1: Physical and chemical properties of urea

Property	Unit	Value
Melting point	°C	133
pH of water solution	pH	7,1-8,4
Density	g/cm ³	1,34
Vapour pressure	hPa	0,1
Thermal decomposition	°C	134

Table A2: Physical and chemical properties of two types of PVOH

Property	Unit	Partially hydrolysed	Fully hydrolysed
		PVOH	PVOH
Melting point	°C	180-190	200-230
pH	pH	4,5-6,5	5,5-7,0
Degree of hydrolysis	%	87-89	98-98,8
Bulk density	kg/m ³	640	640
Viscosity @ 4% solution	cps	45-55	3,5-4,5
Ash content	%	0,5	1,2

Table A3: Physical and chemical properties of paraffin wax compounds

Property	Unit	M3X	M3E	SRW
Melting	°C	60-65	60-66	58-62
Penetration	0,1 mm	17-24	10-18	10-18
Oil content	%	2,4-3,4	1,5 max	1,5 max
Saybolt colour	minutes	10 min	20 min	1,5 max

Table A4: Physical properties of ethylene vinyl acetate (EVA) copolymers

Property	EVA 210	EVA 410	EVA 265	Unit
Melt index	400	500	3,0	dg/min
Vinyl acetate	28	18	28	%
Density at 23°C	951	934	955	g/m ³
Tensile strength	2,8	4,7	29	MPa
Elongation at break	800-1 000	600-900	800-1 000	%
Elastic (tensile) modulus	12	33	28	MPa
Hardness	62	80	83	seconds
Softening point (ring & ball)	82	88	171	°C
Cloud point in paraffin wax	66	66	66	°C

Table A5: Physical and chemical properties of glycerol

Property	Unit	Value
Melting point	°C	18
Solubility	-	Soluble in water
Boiling point	°C	290
Bulk density	kg/m ³	1,26
Vapour density	cps	3,17

Table A6: Suppliers and grades of material used

Material	Supplier	Grade
Ethylene vinyl acetate	Dupont	EVA210
Polyvinyl alcohol	Celanese	Celvol 540
Wax	Sasol Schumann	Paraffin M3X
Urea	Algro Brits	Fertilizer grade
Glycerol	Promark chemicals	CP grade

Appendix B: Specifications of processing and characterisation equipment

The following tables show the specifications of the processing and characterisation equipment used.

Table B1: Processing equipment specifications

Equipment	Uses	Machine & Specification
Two-roll mill	Compounding	Bridge, max. spinning speed 30 r/min Roll space 0,025-0,25 inch
Single-screw extruder	Compounding	Rapra, 25 mm screw diameter Output 5 k/h
Twin-screw co-rotating intermeshing extruder	Compounding	Berstoff, Max output 120 k/h Screw diameter 40 mm Screw speed 0-500 r/min
Injection moulder	Pattern production	Engel, max. clamp force 800 kN Max. pressure 200 bars, Screw diameter 40 mm, Max injection speed 113 mm/s

Table B2: Specifications of characterisation equipment

Equipment	Characterisation parameter	Instrument specification
Three-point test	Mechanical properties: load/deflection, work done, modulus of rupture, Young's modulus of bending	Lloyd instrument: load capacity 5 kN
Impact tester	Mechanical properties: impact strength	Zwick Hammer load 10-40 kpcm
Differential scanning calorimeter	Thermal properties: melting temperature, crystallisation temperature, heat of melting	Perkin Elmer DSC 7
Differential thermal analysis	Thermal properties: melting temperature, heat of melting	Mettler Toledo
Dynamic mechanical analysis	Viscoelastic properties: storage and loss modulus, loss tangent, linear thermal expansion coefficient	Perkin Elmer DMA 7e Modulus: 10^4 to 10^{12} Frequency 0,01 to 51 Hz
Thermogravimetric analysis	Thermal decomposition: mass loss	Mettler Toledo

Appendix C: Processing conditions for compounding and injection moulding

Table C1: Twin-screw extruder compounding trials on EVA-urea-based pattern

	Temperature profile (°C)				Amps	Screw speed
	T ₁ (hopper)	T ₂	T ₃	T ₄ (die)	A	(r/min)
UE 80:15:5	106	102	103	105	15	102
UE 80:10:10	101	102	103	105	12	106
UE 80:5:15	102	103	104	105	18	108
UE 75:20:5	101	102	104	107	15	105
UE 75:15:10	102	103	104	105	18	107
UE 75:10:15	106	107	103	108	12	106
UE 70:25:5	109	103	102	108	18	107
UE 70:20:10	105	105	104	109	15	105
UE 70:15:15	102	103	104	105	18	107

Table C2: Two-roll mill compounding conditions of PVOH urea-based patterns

Temperature profile (°C)		(r/min)
T ₁ (Roll 1)	T ₂ (Roll 2)	
110	110	15

Table C3: Overall injection moulding conditions of urea-based compounds

Urea moulding compounds	Temperature profile (°C)				Injection speed (mm/s)	Cooling time (s)	Injection pressure (bar)
	T ₁ (hopper)	T ₂	T ₃	T ₄ (die)			
UEVA	100	100	100	105	25	15	90
UP8	100	103	100	106	20	15	90
UP4	105	105	105	110	25	15	90
Cooked (benchmark)	90	90	95	100	20	15	90

Appendix D: Experimental procedure for producing cooked urea-based moulding compounds

1. Add 30 l of water and 150 kg of urea to each of the two pots.
2. Heat content to 125°C.
3. Parallel to the above; add 40 l of water, 15 kg of Moviol 40-88 (PVA), 10 kg of urea and 10 l of spirits to the small pot and heat to 90°C.
4. When the urea and water mixture reaches 125°C, add 125 ml of antifoam (Silfoame 212F).
5. When the urea and water mixture reaches 130°C, add half of the contents of the small pot to each of the two bigger pots.
6. Heat to 150°C.
7. Add 800 ml of glycerine and 1,5 kg of Sasol A1 wax.
8. Heat to 164°C and tap off.

Appendix E: Property values of cooked urea moulding compound (benchmark)

Property	Unit	Value	Standard deviation	Method
Mechanical properties				
Maximum load	N	61,2	2,12	ASTM D790
Maximum deflection	mm	1,58	0,16	ASTM D790
Flexural stress	MPa	37,0	1,3	ASTM D790
Flexural strain	%	0,92	0,09	ASTM D790
Modulus of elasticity	GPa	8,5	0,36	ASTM D790
Fracture energy	mJ	67,7	12,6	ASTM D790
Charpy impact strength	kJ/m ²	0,56	0,13	ISO 180
Thermal properties				
Melting temperature	°C	107,0	-	DSC
Mass loss at temperature:	°C			TGA
95% Mass loss		418		
97% Mass loss		472		
Flow properties				
Melt flow index	dg/min@110°C	44,5	6,87	ASTM 1238
Thermal mechanical properties				
Linear thermal expansion coefficient	10 ⁻⁶ °C	120,6	-	TMA
Vicat softening temperature	°C	57,2		TMA
Density @ 25 °C	kg/m ³	1120		

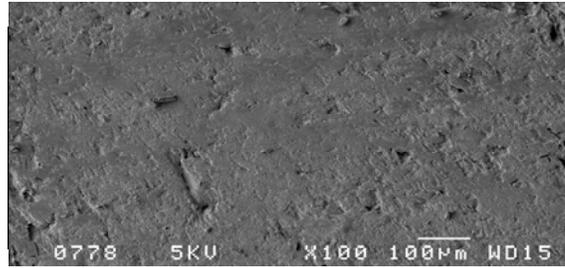


Figure E1: SEM surface photograph of cooked urea moulding compound

Appendix F: Mechanical property data on urea moulding compounds

Table F1: Charpy impact test data for PVOH (80 phr glycerol) moulding compounds

Urea:PVOH8:wax	Z₀ ± SZ₀ (N)	W_h ± SW_h (mm)	T_s ± ST_s (mm)	F ± SF (J)	I_s ± SI_s (kJ/m²)
90:5:5	1,33	4,194 ± 0,011	10,068 ± 0,013	5,39 ± 0,50	0,96 ± 0,12
85:10:5	1,33	4,178 ± 0,010	10,062 ± 0,008	14,6 ± 0,82	3,16 ± 0,20
80:15:5	1,33	4,192 ± 0,004	10,090 ± 0,025	23,4 ± 3,49	5,24 ± 0,82
85:5:10	1,33	4,168 ± 0,017	10,038 ± 0,026	4,14 ± 0,38	0,67 ± 0,09
80:10:10	1,33	4,174 ± 0,013	10,068 ± 0,008	7,73 ± 0,33	1,52 ± 0,07
75:15:10	1,33	4,182 ± 0,011	10,076 ± 0,005	14,5 ± 2,42	3,12 ± 0,58
80:5:15	1,33	4,160 ± 0,012	10,070 ± 0,100	3,17 ± 0,78	0,44 ± 0,19
75:10:15	1,33	4,140 ± 0,025	10,034 ± 0,032	5,87 ± 0,98	1,09 ± 0,24
70:15:15	1,33	4,152 ± 0,019	10,048 ± 0,016	10,2 ± 0,91	2,21 ± 0,22

Table F2: Charpy impact test data for PVOH (40 phr glycerol) moulding compounds

Urea:PVOH:wax	$Z_0 \pm SZ_0$ (N)	$W_h \pm SW_h$ (mm)	$T_s \pm ST_s$ (mm)	$F \pm SF$ (J)	$I_s \pm SI_s$ (kJ/m ²)
90:5:5	1,33	4,130 ± 0,015	10,006 ± 0,015	4,81 ± 0,64	0,84 ± 0,15
85:10:5	1,33	4,180 ± 0,012	10,096 ± 0,026	5,12 ± 0,49	0,90 ± 0,12
80:15:5	1,33	4,180 ± 0,005	10,112 ± 0,031	8,41 ± 0,30	1,67 ± 0,10
85:5:10	1,33	4,193 ± 0,014	10,064 ± 0,026	3,65 ± 0,72	0,55 ± 0,17
80:10:10	1,33	4,190 ± 0,017	10,096 ± 0,017	5,06 ± 0,60	0,88 ± 0,14
75:15:10	1,33	4,182 ± 0,025	10,084 ± 0,005	7,47 ± 2,08	1,46 ± 0,50
80:5:15	1,33	4,204 ± 0,028	10,086 ± 0,023	3,47 ± 0,45	0,50 ± 0,10
75:10:15	1,33	4,204 ± 0,029	10,082 ± 0,024	5,84 ± 0,31	1,06 ± 0,07
70:15:15	1,33	4,144 ± 0,009	10,068 ± 0,048	7,34 ± 0,44	1,44 ± 0,10

Table F3: Charpy impact test data for EVA moulding compounds

Urea:EVA:wax	$Z_0 \pm SZ_0$ (N)	$W_h \pm SW_h$ (mm)	$T_s \pm ST_s$ (mm)	$F \pm SF$ (J)	$I_s \pm SI_s$ (kJ/m ²)
80:15:5	1,33	4,184 ± 0,027	10,042 ± 0,058	4,746 ± 0,691	0,81 ± 0,16
75:20:5	1,33	4,162 ± 0,001	10,048 ± 0,030	8,433 ± 1,105	1,70 ± 0,27
70:25:5	1,33	4,160 ± 0,007	10,020 ± 0,046	9,630 ± 1,630	1,99 ± 0,39
65:30:5	1,33	4,164 ± 0,005	10,050 ± 0,001	14,14 ± 1,770	3,06 ± 0,43
80:10:10	1,33	4,204 ± 0,015	10,040 ± 0,022	4,214 ± 0,850	0,68 ± 0,20
70:20:10	1,33	4,158 ± 0,003	10,002 ± 0,030	9,453 ± 2,102	1,95 ± 0,51
65:25:10	1,33	4,120 ± 0,007	10,096 ± 0,008	11,51 ± 0,590	2,45 ± 0,14
60:30:10	1,33	4,166 ± 0,011	10,008 ± 0,006	10,43 ± 1,537	2,18 ± 0,36
80:5:15	1,33	4,160 ± 0,021	9,992 ± 0,032	2,235 ± 0,435	0,22 ± 0,11
75:10:15	1,33	4,162 ± 0,083	10,032 ± 0,033	4,550 ± 0,413	0,77 ± 0,10
70:15:15	1,33	4,178 ± 0,015	10,060 ± 0,012	5,648 ± 0,377	1,03 ± 0,09
70:20:15	1,33	4,166 ± 0,011	10,016 ± 0,054	9,806 ± 1,419	2,03 ± 0,13



Table F4: Three-point bending test data for PVOH (80 phr glycerol) moulding compounds

Urea:PVOH:wax	$M_L \pm SM_L$ (N)	$M_D \pm SM_D$ (mm)	$\epsilon_b \pm S\epsilon_b$ (%)	$E \pm SE$ (GPa)	$M_R \pm SM_R$ (MPa)	$W_D \pm SW_D$ (MPa)
90:5:5	55,49 ± 1,12	1,26 ± 0,13	0,0074 ± 0,83	10,07 ± 0,69	33,24 ± 0,72	49,54 ± 10,43
85:10:5	35,91 ± 1,90	3,79 ± 0,29	0,0233 ± 0,21	6,06 ± 0,28	21,54 ± 1,14	107,89 ± 13,92
80:15:5	31,08 ± 0,93	6,89 ± 0,44	0,0404 ± 0,12	4,23 ± 0,28	18,65 ± 0,56	148,55 ± 1,46
85:5:10	60,95 ± 3,11	1,35 ± 0,13	0,0078 ± 0,58	10,14 ± 0,64	36,98 ± 1,76	53,59 ± 8,66
80:10:10	33,76 ± 1,59	2,77 ± 0,16	0,0163 ± 0,07	6,00 ± 0,43	20,26 ± 0,95	71,17 ± 7,71
75:15:10	28,14 ± 1,17	5,69 ± 0,41	0,0333 ± 0,09	3,36 ± 0,46	16,89 ± 0,71	119,19 ± 16,08
80:5:15	60,29 ± 2,13	1,31 ± 0,12	0,0076 ± 0,21	9,06 ± 0,76	36,17 ± 1,28	49,25 ± 8,18
75:10:15	37,04 ± 4,97	2,91 ± 0,65	0,0271 ± 0,24	6,03 ± 0,67	22,22 ± 2,98	72,99 ± 12,38
70:15:15	30,92 ± 0,80	4,98 ± 0,66	0,0292 ± 0,19	4,04 ± 0,35	18,55 ± 0,48	113,95 ± 23,13



Table F5: Three-point bending test data for PVOH (40 phr glycerol) moulding compounds

Urea:PVOH:wax	$M_L \pm SM_L$ (N)	$M_D \pm SM_D$ (mm)	$\epsilon_b \pm S\epsilon_b$ (%)	$E \pm SE$ (GPa)	$M_R \pm SM_R$ (MPa)	$W_D \pm SW_D$ (MPa)
90:5:5	79,60± 2,21	1,40± 0,12	0,0074± 0,15	11,39±0,26	47,76± 1,33	71,44± 11,43
85:10:5	61,72± 1,93	2,22± 0,36	0,0134± 0,12	9,08± 0,82	37,03 ± 1,16	97,47 ± 11,92
80:15:5	61,85± 1,90	3,56± 0,13	0,0208± 0,10	8,12± 0,47	37,11± 1,14	155,50±1,46
85:5:10	81,62± 5,5	1,55 ± 0,27	0,0091± 0,17	11,32± 0,95	48,97± 3,33	84,38 ± 8,66
80:10:10	61,77± 1,70	1,29± 0,28	0,0076 ± 0,14	10,38± 0,86	37,06± 1,02	51,22± 7,71
75:15:10	48,07± 2,84	2,27 ± 0,12	0,0133± 0,50	6,68± 0,60	28,84± 1,70	72,30± 16,08
80:5:15	81,20± 3,56	1,37 ± 0,28	0,0080± 0,10	10,65± 0,82	48,72± 2,13	66,04± 8,18
75:10:15	63,13± 1,54	2,23± 0,12	0,0136± 0,07	9,16± 0,64	37,87± 0,92	80,26± 12,38
70:15:15	45,40± 2,99	2,82± 0,54	0,0165± 0,10	5,24± 0,43	27,24± 1,80	86,58± 23,13



Table F6: Three-point bending test data for EVA moulding compounds

Urea:EVA:wax	$M_L \pm SM_L$ (N)	$M_D \pm SM_D$ (mm)	$\epsilon_b \pm S\epsilon_b$ (%)	$E \pm SE$ (GPa)	$M_R \pm SM_R$ (MPa)	$W_D \pm SW_D$ (MPa)
80:15:5	29,45±1,58	0,62± 0,04	0,0036± 0,21	7,71±1,13	17,67± 0,95	9,53± 0,70
75:20:5	16,84± 0,27	1,17± 0,06	0,0069± 0,33	3,83± 0,75	10,11 ± 0,16	12,90 ± 0,88
70:25:5	13,74± 0,14	1,77± 0,09	0,0104± 0,50	2,21± 0,08	8,25± 0,08	16,06±0,66
65:30:5	11,65± 0,34	2,52± 0,09	0,0148± 0,50	1,26± 0,04	6,99± 0,20	20,79 ± 1,16
80:10:10	29,93± 1,58	0,54± 0,02	0,0031± 0,14	8,51± 0,57	17,96± 0,95	8,50± 0,59
70:20:10	21,23± 0,34	0,90± 0,09	0,0081± 0,50	3,43± 0,77	9,15± 0,41	14,37± 1,03
65:25:10	15,25± 0,69	1,39± 0,05	0,0089± 0,03	1,86± 0,16	8,25± 0,08	18,05± 1,25
60:30:10	11,62± 0,15	2,25± 0,03	0,0171± 0,17	1,24± 0,16	7,42± 0,15	23,63± 0,79
80:5:15	12,26± 0,05	2,95± 0,38	0,0066± 0,10	6,30± 0,9	18,43± 1,10	7,84± 0,64
75:10:15	24,57± 1,46	0,75± 0,11	0,0108± 0,08	4,61± 0,57	13,92± 0,36	11,84± 0,58
70:15:15	23,20± 0,60	1,20± 0,08	0,0256± 0,06	1,76± 0,34	12,04± 0,87	19,84± 1,89
65:20:15	17,13± 0,42	2,86±0,10	0,0356± 0,06	1,22± 0,08	10,28± 0,25	22,24± 1,18

Appendix G: Matlab script for performing two-way ANOVA

Appendix G1: Matlab script file for performing two-way ANOVA on the Charpy impact test data obtained with urea-wax- PVOH (80 phr of glycerol) compounds

```
%----- Script file for 2-way analysis of impact strength-----
%
% Charpy data for urea-PVOH-wax
% PVOH contains 80phr glycerol
%
% Response variable = ln(Charpy impact (unnotched)in kJ/m2)
%
% Hilary Rutto 9 April 2006
% Last time modified 9 April 2006
%
% *****
%
%
% The purpose is to determine the effect of wax and polymer content on the
% Charpy impact strength of the pattern material,
%
% Three different wax levels (5%, 10% & 15%) were considered (columns),
% Three different polymer levels (5%, 10% & 15%) were considered (rows)
%
% Five replicates at each composition were tested
% Thus there are a total of 15 rows and three columns in the data set
%
% Initialize the number of wax levels:
PVOH = [0,050 0,050 0,050 0,050 0,050 0,050 0,050 0,050,
        0,050 0,050 0,050 0,050 0,050 0,050 0,050 0,100,
        0,100 0,100 0,100 0,100 0,100 0,100 0,100 0,100,];
```

```
0,100 0,100 0,100 0,100 0,100 0,100 0,150 0,150,,,
0,150 0,150 0,150 0,150 0,150 0,150 0,150 0,150,,,
0,150 0,150 0,150 0,150 0,150];
```

```
%
```

```
wax = [0,0500 0,0500 0,0500 0,0500 0,0500 0,1000 0,1000 0,1000,,,
0,1000 0,1000 0,1500 0,1500 0,1500 0,1500 0,1500 0,0500,,,
0,0500 0,0500 0,0500 0,0500 0,1000 0,1000 0,1000 0,1000,,,
0,1000 0,1500 0,1500 0,1500 0,1500 0,1500 0,0500 0,0500,,,
0,0500 0,0500 0,0500 0,1000 0,1000 0,1000 0,1000 0,1000,,,
0,1500 0,1500 0,1500 0,1500 0,1500];
```

```
% Enter the experimental Charpy data
```

```
%
```

```
CharpyUP8 = [-0,113 -0,138 0,094 -0,143 0,075 -0,514 -0,485,,,
-0,402 -0,445 -0,189 -1,019 -1,904 -0,519 -0,643 -0,559,,,
1,089 1,170 1,086 1,235 1,164 0,421 0,331 0,450,,,
0,440 0,451 -0,189 -0,150 0,281 0,122 0,272 1,814,,,
1,664 1,783 1,514 1,455 0,914 1,362 1,009 1,086,,,
1,257 0,804 0,825 0,722 0,817 0,578];
```

```
%
```

```
varnames = {'Wax level', 'PVOH level'}
```

```
% The ANOVA table has columns for the sums of squares, degrees-of-freedom,  
% mean squares (SS/df), F statistics, and p-values,
```

```
%
```

```
% Generate the ANOVA table for the Charpy data
```

```
[p,tbl,stats] = ANOVAn(CharpyUP8,{wax PVOH},2,3,varnames);
```

```
%
```

Appendix G2: Matlab script file for performing multiple linear regression on the Charpy impact test data obtained with urea-wax-PVOH (80 phr of glycerol) compounds

```
%  
%----- Script file for 2-way analysis of impact strength-----  
%  
% Charpy data for urea-PVOH-wax  
% PVOH contains 80phr glycerol  
%  
% Charpy impact (unnotched)in kJ/m2  
%  
% Hilary Rutto 9 April 2006  
% Last time modified 9 April 2006  
%  
% *****  
%  
%  
% The purpose is to determine the effect of wax and polymer content on the  
% Charpy impact strength of the pattern material,  
%  
% Three different wax levels (5%, 10% & 15%) were considered (columns),  
% Three different polymer levels (5%, 10% & 15%) were considered (rows)  
%  
% Five replicates at each composition were tested  
% Thus there are a total of 15 rows and three columns in the data set  
%  
% Now do linear regression  
% Data set for linear regression  
% Data matrix has a column of ones, and then one column of values for each  
% of the predictor variables, The column of ones is necessary for  
% estimating the y-intercept of the linear model, The last column gives the
```



% Charpy impact strength values

%

Data =[1 0,050 0,0500 -0,113

1 0,050 0,0500 -0,138

1 0,050 0,0500 0,094

1 0,050 0,0500 -0,143

1 0,050 0,0500 0,075

1 0,050 0,1000 -0,514

1 0,050 0,1000 -0,485

1 0,050 0,1000 -0,402

1 0,050 0,1000 -0,445

1 0,050 0,1000 -0,189

1 0,050 0,1500 -1,019

1 0,050 0,1500 -1,904

1 0,050 0,1500 -0,519

1 0,050 0,1500 -0,643

1 0,050 0,1500 -0,559

1 0,100 0,0500 1,089

1 0,100 0,0500 1,170

1 0,100 0,0500 1,086

1 0,100 0,0500 1,235

1 0,100 0,0500 1,164

1 0,100 0,1000 0,421

1 0,100 0,1000 0,331

1 0,100 0,1000 0,450

1 0,100 0,1000 0,440

1 0,100 0,1000 0,451

1 0,100 0,1500 -0,189

1 0,100 0,1500 -0,150

1 0,100 0,1500 0,281

1 0,100 0,1500 0,122

1 0,100 0,1500 0,272



```
1 0,150 0,0500 1,814
1 0,150 0,0500 1,664
1 0,150 0,0500 1,783
1 0,150 0,0500 1,514
1 0,150 0,0500 1,455
1 0,150 0,1000 0,914
1 0,150 0,1000 1,362
1 0,150 0,1000 1,009
1 0,150 0,1000 1,086
1 0,150 0,1000 1,257
1 0,150 0,1500 0,804
1 0,150 0,1500 0,825
1 0,150 0,1500 0,722
1 0,150 0,1500 0,817
1 0,150 0,1500 0,578
];
%
% Set up the linear regression model
%
X = Data(:,1:3);
y = Data(:,4);
[b,bint,r,rint,stats] = regress(y,X);
%
% The y-intercept is b(1)
% It corresponds to the column index of the column of ones
%
% The elements of the vector stats are the regression R2 statistic, the F
% statistic (for the hypothesis test that all the regression coefficients
% are zero), and the p-value associated with this F statistic,
%
stats
%
```



% Scatter plot for the residuals

% The scatter plot shows the residuals plotted in case order (by row),

% The error bars indicate 95% confidence intervals about these residuals

% Outlier observation have error bars that do not cross the zero reference line

`rcoplot(r,rint)`

%

Appendix H: Experimental procedure for measuring density using Archimedes' principle

Calculation of density using Archimedes' principle

1. Mass of the liquid = [mass of liquid in pycnometer + liquid – mass of pycnometer]
2. Mass of undispersed immersed liquid = [mass of liquid in pycnometer + polymer – mass of polymer blend – mass of pycnometer]
3. Mass of displaced immersed liquid = [mass of liquid in pycnometer – mass of undispersed immersed liquid]
4. Volume of the polymer blend = [mass of displaced liquid/theoretical density of liquid]
5. Density of the polymer blend = [mass of dry polymer blend/volume of the polymer blend]